Vol. XXII May, 1945 No. 3

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CEREAL CHEMISTRY

Published bi-monthly by the American Association of Cereal Chemists
at Prince and Lemon Sts., Lancaster, Pa.

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Entered as second-class matter March 3, 1932, at the post office at Lancaster, Pa., under the act of August 24, 1912.

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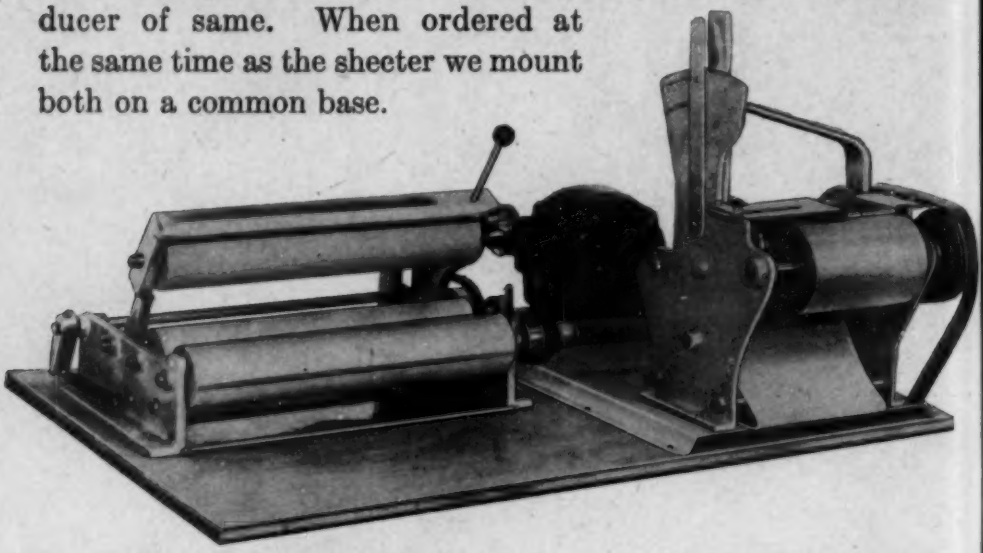

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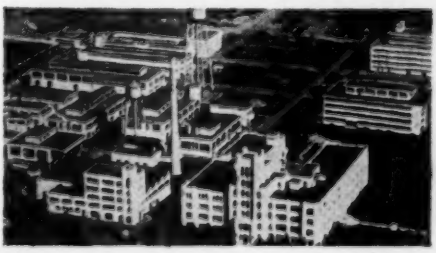

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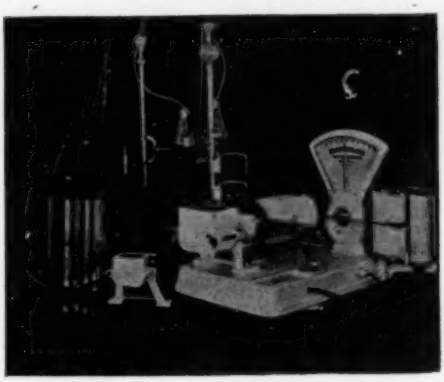

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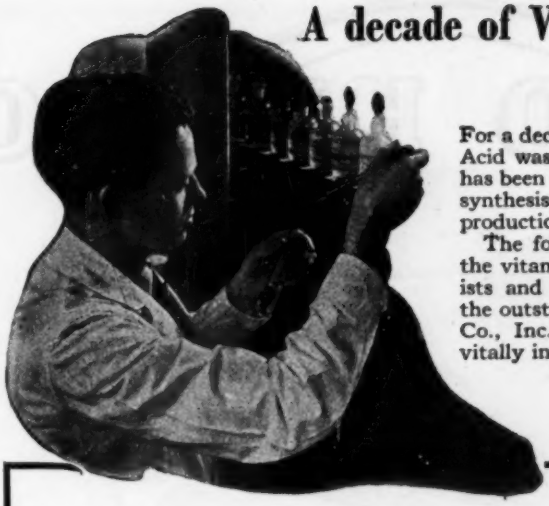

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1940
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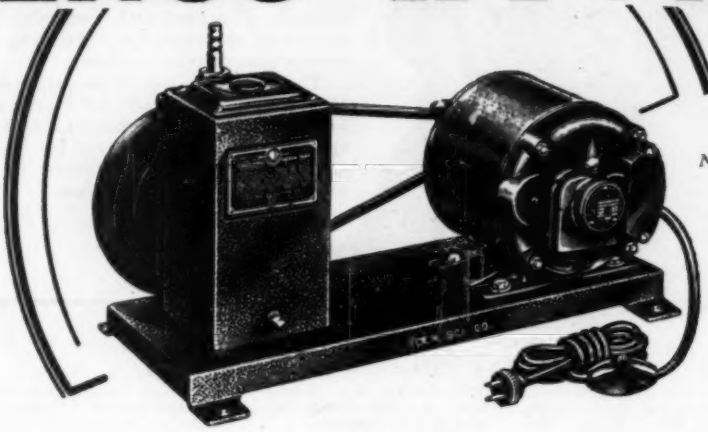

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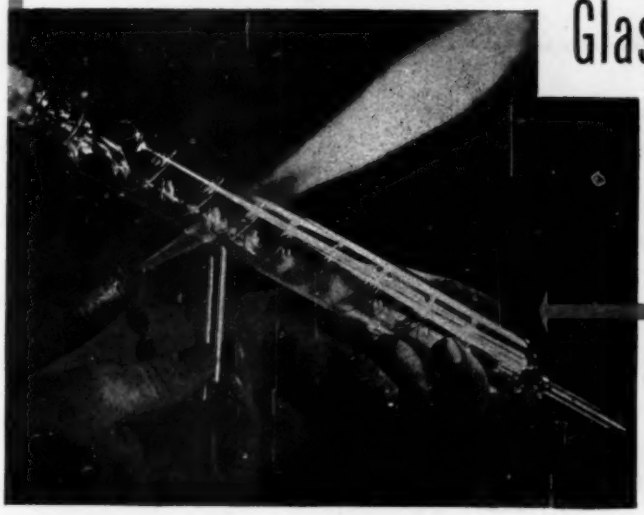

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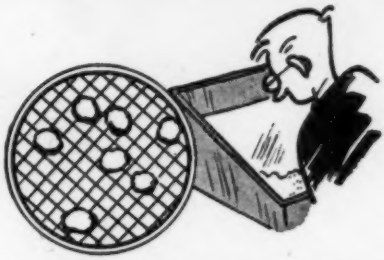

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CEREAL CHEMISTRY

VOL. XXII MAY, 1945 No. 3

ASCORBIC ACID AND SOME RELATED COMPOUNDS AS OXIDIZING AGENTS IN DOUGHS [1]

R. M. SANDSTEDT and B. D. HITES [2]

Department of Agricultural Chemistry,
Nebraska Agricultural Experiment Station, Lincoln, Nebraska

(Received for publication December 1, 1944)

Jørgensen (1935) found that *l*-ascorbic acid (hereinafter AA), when added to flour doughs, had an action similar to that of bromate. Melville and Shattock (1938) state that in doughs requiring considerable oxidation dehydroascorbic acid (DHA) is a more potent bread improver than AA and is equivalent to bromate on a weight-for-weight basis. They showed that flour contains an oxidase which is capable of oxidizing AA to DHA and explained the oxidizing action of AA as being due to the DHA thus formed.

Feaster and Cathcart (1941) reported that AA itself was equivalent to bromate on a weight-for-weight basis. They found that *d*-ascorbic acid was ineffective as a dough improver. Cathcart and Edelmann (1944) state that about one and one-half times as much AA as bromate is required to give equivalent effects in baking.

Elion (1944) reported that compounds having an enediol group adjacent to a carbonyl group were found not only to inhibit papain but also to act as chemical flour improvers. He used *reductone* as a specific example.

In this laboratory we have had occasion to test reductone and some of the analogs of AA as oxidizing agents in doughs and have found that they had little action. Since Melville and Shattock found that the oxidizing action of AA was due to the enzymatic production of DHA, it was assumed that the ascorbic acid oxidase of flour was not capable of oxidizing these analogs. However, Johnson and Zilva (1937) showed that cucumber ascorbic acid oxidase was able to attack the analogs of AA, the rate of oxidation being dependent on the stereochemical structure; *d*-arabo-ascorbic, *l*-gluco-ascorbic, and *l*-galacto-ascorbic acids were oxidized at about the same rate as AA,

[1] Published with the approval of the Director as paper No. 365, Journal Series, Nebraska Agricultural Experiment Station.

[2] With the technical assistance of Virginia A. Schon and Vernard W. Unruh.

whereas the *d*-ascorbic and *l*-arabo-ascorbic acids were attacked more slowly and *d*-gluco-ascorbic acid still more slowly. Snow and Zilva (1938) showed that the cucumber ascorbic acid oxidase also would oxidize such compounds as reductic acid and reductone.

Crook (1941) gives a review of the literature concerning the enzymatic oxidation of AA and enzymatic reduction of DHA.

A study of the action of AA, of some of its analogs, and of reductone in doughs and in flour extracts was undertaken in order to attempt to explain the differences between the action of these compounds in bread doughs. It was thought that such a study might lead to a better understanding of some of the reactions involved in dough oxidation.

Materials and Methods

Reagents. Kellie and Zilva (1935) demonstrated that for work with AA all reagents must be prepared with distilled water which has been redistilled from glass. Butler, Cushman, and MacLachlan (1943) also emphasized the necessity of using glass-distilled water and stated that all reagent vessels should be rinsed with such water. This precaution is exceedingly important if standard solutions of AA are allowed to stand for a few minutes before use, as is usually the case in preparing reference curves for photometric determinations. It is not so important that glass-distilled water be used in making flour extracts since the flour proteins (or other flour constituents) apparently form "inactive" complexes with the metals.

The *d*-gluco-ascorbic acid, the sodium salt of *d*-arabo-ascorbic acid, and reductone were made available through the courtesy of Wallerstein Laboratories, and the *l*-ascorbic acid and *d*-arabo-ascorbic acid (*d*-isoascorbic acid) through the courtesy of Hoffmann-LaRoche, Inc. A portion of the reductone was repurified by sublimation under reduced pressure at 125°C (Snow and Zilva, 1938). *d*-Gluco-ascorbic acid was shown by Johnson and Zilva (1937) to be more slowly oxidized than AA by the ascorbic acid oxidase of cucumber. *d*-Arabo-ascorbic acid is particularly interesting for comparative purposes since Johnson and Zilva showed that it was oxidized at about the same rate as AA.

Dehydroascorbic acid, the oxidized analogs (corresponding to DHA), and oxidized reductone were prepared by oxidation with iodine in water solution; the resulting iodide was not removed. For the studies of reactions in flour extracts, DHA (with most of the iodide removed) also was prepared in solid form by the Hirst method as reported by Crook and Morgan (1944). The DHA is hygroscopic and must be stored in a desiccator.

Flour. The flours used for the work reported in this paper were

an unbleached patent, two first clears, and two second clears. These were all commercial flours, freshly milled from hard winter wheat. They were kept in cold storage (5°) to keep changes due to aging at a minimum. The baking results reported were obtained on a first clear. Similar relationships between the oxidizing effects of the compounds related to AA were obtained on the patent and second clear flours.

The Baking Method. The baking method was the micromethod as modified for use in this laboratory (Sandstedt and Fortmann, 1944). For bakes involving other than a 3-hour fermentation, the sugar in the formula was adjusted to give loaves with crust color similar to that obtained by a 3-hour fermentation with 5% sugar. In comparing oxidizing effects, the ascorbic analogs and reductone were used in proportion to their molecular weights.

Flour Extracts. The 1 : 2 flour extracts were prepared in a manner similar to the method described by Baker, Parker, and Mize (1943); 150 g flour was added to 300 ml ice-cold water (glass-distilled) in a Waring Blendor.

Apparently the metal dissolved from the stainless steel blades of the Waring Blendor is adequately "inactivated" by the flour proteins, since in several trials extracts made by stirring with glass and with the Waring Blendor gave similar AA oxidation curves. The Waring Blendor is preferred as it permits the more ready preparation of extracts in the absence of oxygen. However, glass-distilled water alone stirred in the Waring Blendor takes up enough metal to increase materially the rate of oxidation of AA.

The Blendor was operated for 5 minutes under a bell jar *in vacuo*. The extract was separated by centrifuging for two 10-minute intervals in a Sorvall angle centrifuge. Three or four extractions were necessary in order to obtain enough extract for the series of determinations for one reaction curve. These extracts were used very shortly after preparation, since Crook and Hopkins (1938) and Powers, Lewis, and Dawson (1944) have shown that some of the enzymes responsible for the oxidation of AA and reduction of DHA are quite unstable in water solution. The pH of the extracts was approximately 6.0; the buffering effect of the proteins was great enough so that the AA and GSH additions (5 mg/100 ml) produced no great change in pH.

Boiled Extracts. Flour reducing substances are rapidly lost when extracts are brought to boiling temperature. In order to minimize this loss, the extracts were brought to a boil as rapidly as possible; boiling was continued for 5 minutes. The loss of reducing value and the reactions with AA were similar for extracts boiled in an atmosphere

of CO_2 and for those boiled in air; accordingly, the boiled extracts used in this study were boiled in air.

Analysis for Ascorbic Acid and Its Analogs. The analogs of AA, like AA itself, are oxidized by 2,6-dichlorophenolindophenol. Accordingly, either an indophenol titration or Morell's (1941) photometric indophenol method for AA in plant materials may be used for the determination of AA and its analogs in the flour extracts. In this investigation both methods were used in the presence of 1.5% metaphosphoric acid.

A Coleman Model 10 spectrophotometer was used for the spectrophotometric method. The extracts used in making the standard reference curves corresponded exactly to those used in making the determinations. When making determinations on solutions containing DHA prepared by iodine oxidation, it is essential that the reference curve be made on extracts containing an equivalent quantity of iodide.

Reductone. Reductone is more slowly oxidized by indophenol than are the ascorbic analogs (Snow and Zilva, 1938); accordingly, when reductone was used the reaction was allowed to proceed 5 minutes before the spectrophotometer was read.

Dehydroascorbic Acid. Dehydroascorbic acid was determined as AA after reduction with H_2S and the removal of the H_2S with CO_2 under reduced pressure. According to Penney and Zilva (1943), the H_2S method may not give the absolute value for DHA; however, it does give quite reliable values which serve the purposes of the present paper.

Sulfhydryls. The nitroprusside test for sulfhydryls as described by Meyers and Working (1944) was used. PRECAUTION: It is important that the nitroprusside be *freshly* prepared; fresh solutions must be made up at intervals during the day.

Determination of Total Reducing Value of Flour Extracts. The iodine titration method proposed by Stevens (1938) for the estimation of AA in citrus juices was used for the determination of total reducing value, including added AA, of the flour extracts. N/1,000 iodine was used. "The procedure of adding an excess of iodine, then an excess of thiosulfate, followed by titration of excess thiosulfate," gives excellent end-points in centrifuged, but otherwise unclarified, flour or dough extracts. However, it is essential that the excess iodine be approximately a constant quantity (in these studies 4.0 ml of N/1,000 iodine was used), since the amount of oxidation produced by iodine varies with the amount of excess; however, this does not seem to be a critical factor if AA is present.

Reactions in Flour Extracts. For studying the reactions of AA (or its analogs) the desired quantity of AA (or the analog) was added

to 400 ml of 1 : 2 extract at 30°C. The mixture was stirred vigorously to supply molecular oxygen during the entire course of the reaction. Octyl alcohol may be used to prevent foam formation, although it is not necessary. The quantity of reduced compound was determined on aliquots taken at suitable intervals.

After most of the work reported in this paper had been completed, it was found that light intensity was a factor in determining the rate of AA oxidation induced by the catalysts which are found in *boiled* flour extracts. Fortunately the light in the laboratory was reasonably constant and the rate of oxidation of AA in *unheated* extracts was not seriously affected by such small differences in light intensity as did occur. The work reported comparing the reaction rates of AA with those of its analogs and reductone was carried out in the dark.

Baking Results Using Ascorbic Acid and Related Compounds

The oxidizing effect of AA as compared to that of bromate is shown by loaves 1 to 4 in Figure 1. The marked oxidizing action of AA is evident, but, as was shown by Melville and Shattock (1938), it was not so effective as bromate.

The reductone and the analogs were used in proportion to their molecular weights. Loaves 5 to 8 of Figure 1 show the comparative effectiveness of *d*-arabo-ascorbic, *d*-gluco-ascorbic, reductone, and sodium *d*-arabo-ascorbate. The ineffectiveness of these compounds may be judged by comparison with loaves 1, 2, and 4. Reductone, whether repurified or not, and *d*-gluco-ascorbic acid produced no oxidizing effect; in fact, reductone seemed to have a slight reducing effect; *d*-arabo-ascorbic acid and its salt, sodium *d*-arabo-ascorbate, had some slight oxidizing action. The loaves baked from doughs containing five times as much of these compounds (Figure 2) illustrate even more forcefully the slight oxidizing action of *d*-arabo-ascorbic acid and of its sodium salt, the almost complete ineffectiveness of *d*-gluco-ascorbic acid, and the slight reducing action of reductone. Comparison of loaves in Figure 1 with those in Figure 2 shows that a five-fold increase in quantity produced little additional effect.

The Use of Oxidized Compounds. Melville and Shattock (1938) showed the increase in effectiveness of AA after its oxidation to DHA and its complete lack of action after its conversion to diketogulonic acid. The loaves pictured in Figure 3 show the comparative oxidizing action of oxidized AA and of its oxidized analogs. The increased effectiveness of these compounds after oxidation is apparent. However, used at equivalent levels the oxidized analogs were not so effective as DHA or even so effective as AA. The loaves containing oxidized reductone indicated inappreciable oxidizing action.

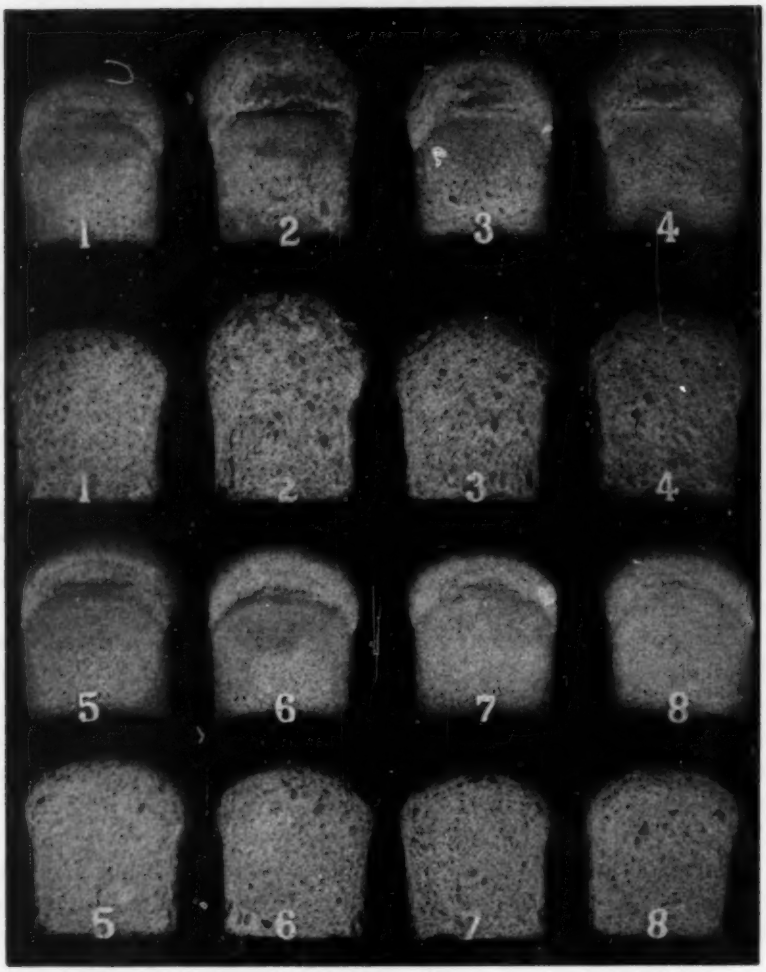


Fig. 1. Comparison of the oxidizing effect of ascorbic acid and some structurally closely related compounds in unbleached first clear doughs.

Loaf 1—check, no oxidation—volume 132 cc.
Loaf 2—2 mg % of bromate—volume 186 cc.
Loaf 3—2 mg % of *l*-ascorbic acid—volume 154 cc.
Loaf 4—4 mg % of *l*-ascorbic acid—volume 170 cc.
Loaf 5—4 mg % of *d*-arabo-ascorbic acid—volume 141 cc.
Loaf 6—4.7 mg % of *d*-gluco-ascorbic acid—volume 135 cc.
Loaf 7—2 mg % of reductone—volume 135 cc.
Loaf 8—4.9 mg % of sodium-*d*-arabo-ascorbate—volume 135 cc.

The increased oxidation obtained by the use of the oxidized analogs over that obtained with the reduced compounds indicates that much of the deficiency in the action of the unoxidized compounds was due to the limited ability of the oxidases of the flour to promote their oxidation. It is obvious that this is not the complete explanation of their ineffectiveness, since the oxidized analogs were not so effective as DHA.

Feaster and Cathcart (1941) observed that flours seemed to have more tolerance for AA than for bromate. The use of greater quantities than about 4 mg % of AA in doughs made from the hard winter wheat flours used for the present work produced much less change in bread characteristics than was anticipated. Figure 4 shows loaves obtained by the use of 20 mg % of AA and 24 mg % of DHA. The loaf containing 20 mg % AA (loaf 1, Figure 4) showed more oxidation than that containing 4 mg % (loaf 4, Figure 1), but the increase was slight in comparison to the drastic effect which would be obtained by use of similar quantities of such oxidizing compounds as bromate,

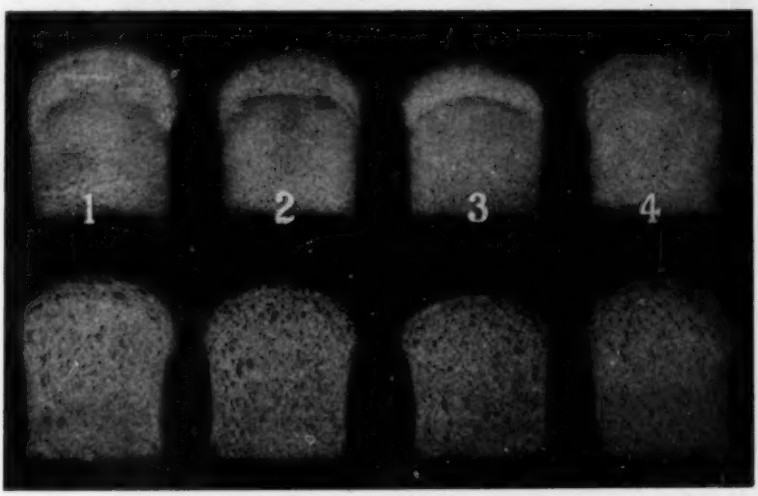
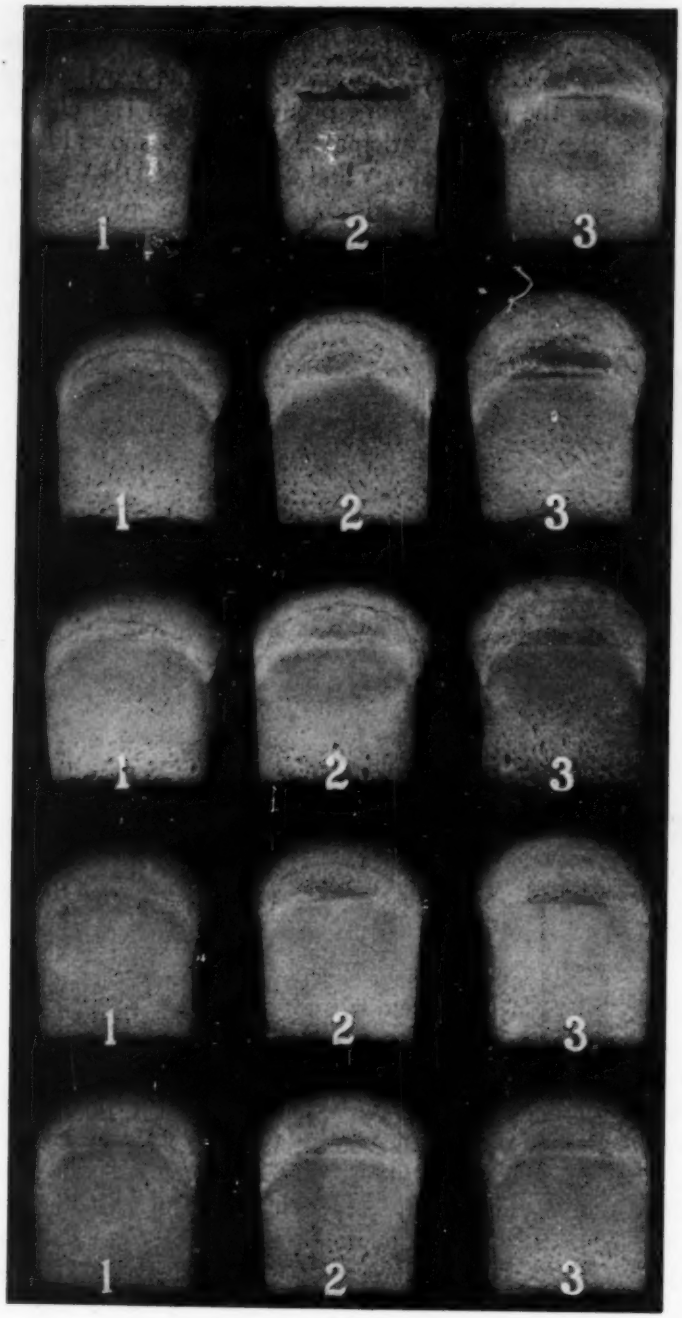


Fig. 2. Further comparison of the oxidizing action of compounds related to ascorbic acid.
Loaf 1—20 mg % of *d*-arabo-ascorbic acid—volume 137 cc.
Loaf 2—23 mg % of *d*-gluco-ascorbic acid—volume 133 cc.
Loaf 3—10 mg % of reductone—volume 128 cc.
Loaf 4—25 mg % of sodium-*d*-arabo-ascorbate—volume 135 cc.

iodate, or chlorite. Apparently the quantity of added AA was not the limiting factor in the oxidation of these doughs.

The overoxidation produced by 9.6 mg % and 24 mg % of DHA (Figures 3 and 4) is further indication that one of the important factors in the dough oxidation with AA was the ascorbic acid oxidase of the flour. Perhaps variation in ascorbic acid oxidase from one flour to another would explain the differences in comparative oxidations by AA and by bromate obtained in different laboratories (compare Melville and Shattock, 1938, Feaster and Cathcart, 1941, and the present paper).

Mixing Effects on Oxidation by Ascorbic Acid. The oxidation of AA by ascorbic acid oxidase is dependent on a supply of molecular



Dehydro-*l*-ascorbic acid. Loaf volumes 145,176,170

Dehydro-*d*-arabo-ascorbic acid. Loaf volumes 136,152,167

Dehydro-*d*-arabo-ascorbate. Loaf volumes 131,140,147

Dehydro-*d*-gluco-ascorbic acid. Loaf volumes 130,137,142

Oxidized reductone. Loaf volumes 130,134,136

Fig. 3. Comparison of the oxidizing action of dehydroascorbic acid with the oxidizing action of the oxidized analogs and reductone. Molecular equivalents to 1 mg %, 4 mg %, and 8 mg % of *l*-ascorbic acid were used.

oxygen. The effectiveness of the oxidation with AA in doughs then should be dependent on the amount of oxygen beaten into the dough during the mix. The upper row of loaves shown in Figure 5 indicates that this is true; the bread baked from the hand-mixed dough showed little oxidation, whereas that from the 1, 2, and 3 minute machine-mixed doughs showed increasing oxidation. Changes in bread characteristics are expected with changes in the mixing time; however, this flour oxidized with DHA (lower row of loaves of Figure 5) showed less mixing response than was shown in the AA loaves. Loaves

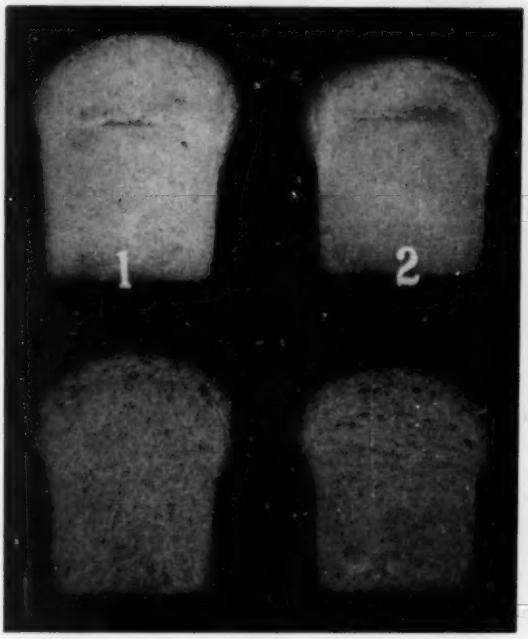


Fig. 4. Oxidizing effect of 20 mg % of *l*-ascorbic acid (Loaf 1, volume 172 cc) and 24 mg % of dehydroascorbic acid (Loaf 2, volume 163 cc).

oxidized with 2 mg % bromate showed approximately the same mixing response as those oxidized with 4.8 mg % DHA.

The Effect of Fermentation Time on Oxidation with Ascorbic Acid. Since the ascorbic acid oxidase of the flour seems to be a limiting factor in oxidation by means of AA, it would be expected that the time given for fermentation would be a factor in determining the amount of oxidation obtained and that oxidation with DHA would be effective at shorter periods of fermentation. The loaves shown in Figure 6 indicate such a relationship. Optimum oxidation with 4 mg % AA (2-minute mixing) was obtained by a 3-hour fermentation whereas the

optimum with DHA was obtained by a 2-hour fermentation. This indicates that the rate of oxidation of AA is one limiting factor but that even with DHA oxidation is rather slow, although more rapid than bromate oxidation (it is much less drastic than bromate).

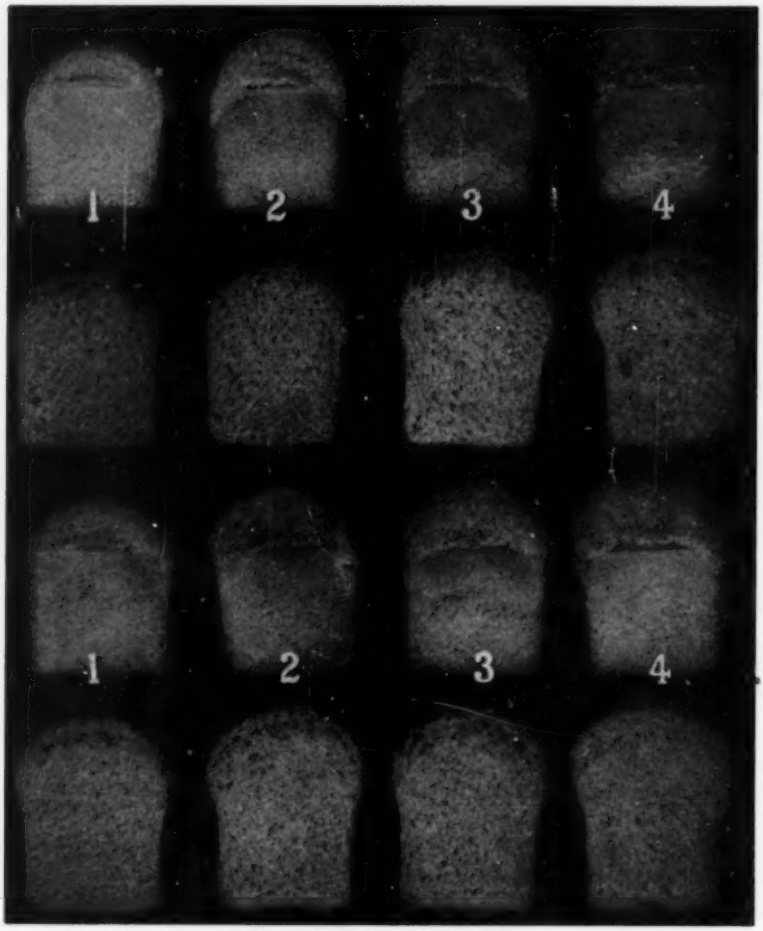


Fig. 5. Effect of severity of mixing on the oxidizing effect produced by 4 mg % of ascorbic acid (above) and by 4.8 mg % of dehydroascorbic acid (below).
Loaf 1—hand mixed, 100 cuts with spatula—volumes: AA 145 cc; DHA 152 cc.
Loaf 2—machine mixed, 1 minute—volumes: AA 155 cc; DHA 175 cc.
Loaf 3—machine mixed, 2 minutes—volumes: AA 164 cc; DHA 171 cc.
Loaf 4—machine mixed, 3 minutes—volumes: AA 178 cc; DHA 174 cc.

Oxidation of Ascorbic Acid in Flour Extracts

In order to facilitate an interpretation of the oxidizing properties of AA and of the other compounds of similar structure, a study was made of their action in flour extracts. Figure 7 shows the course of

oxidation of AA in a 1 : 2 water extract of an unbleached second clear.[3] Curve C shows the data obtained by subtracting the AA, as determined by the indophenol method (curve B), from the total reducing value obtained by iodine titration (curve A); *i.e.*, curve C shows the course of oxidation of the reducing material of the flour extract itself during the reaction period studied.

In some respects this set of oxidation curves for AA in flour extracts is quite similar to the curves shown by Hopkins and Morgan (1936), Crook and Hopkins (1938), and Crook and Morgan (1944) for the

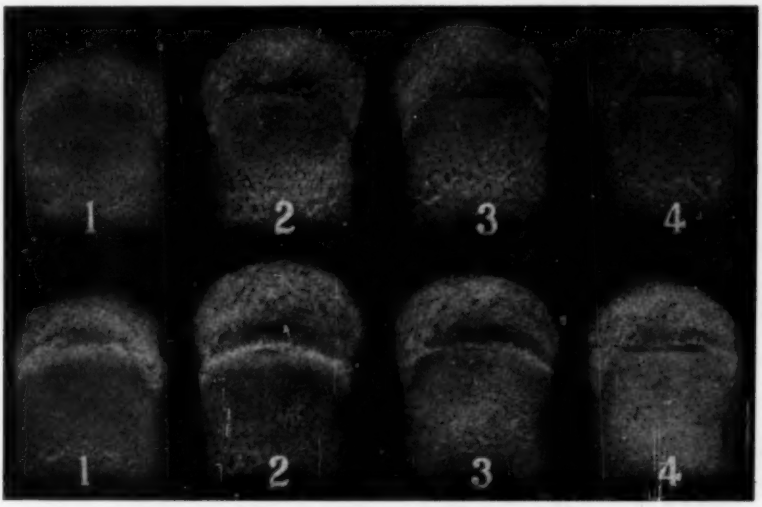


Fig. 6. Effect of fermentation time on oxidation by ascorbic acid and by dehydroascorbic acid Upper row 4 mg % of ascorbic acid. Lower row 4.8 mg % of dehydroascorbic acid.

Loaf 1—1-hour fermentation—volumes: AA 132 cc, DHA 145 cc.
Loaf 2—2-hour fermentation—volumes: AA 167 cc, DHA 190 cc.
Loaf 3—3-hour fermentation—volumes: AA 171 cc, DHA 176 cc.
Loaf 4—5-hour fermentation—volumes: AA 166 cc, DHA 164 cc.

oxidation of glutathione (GSH) by AA in the presence of cauliflower (and cabbage) juice. These authors concluded that when AA and GSH were added to cauliflower juice (containing ascorbic acid oxidase) the AA was wholly protected from oxidation, whereas the GSH was oxidized at exactly the same rate as was AA when alone in the juice. Crook (1941) pointed out that this was not actually a protection from oxidation since the AA was oxidized by the oxidase to DHA which in turn oxidized the GSH at the same rate as it (DHA) was being formed. Perceptible oxidation of the AA began just when a nitroprusside test showed the disappearance of GSH. Hopkins, Morgan,

[3] The pH of this extract was 6.12 before and 5.98 after the AA addition.

and Crook state that under these conditions AA acts as a co-enzyme for the oxidation of GSH.

Interpreted in the light of these investigations, the data shown in Figure 7 indicate that a similar oxidizing and reducing enzyme system may be present in wheat flours, with the flour also furnishing the reducing groups.

In the second clear flour extract (Figure 7) there was the apparent absence of oxidation of AA for the first 20 minutes (the plateau at the beginning of curve B) until certain reducing groups in the extract had disappeared. There was then a rapid oxidation of AA. The

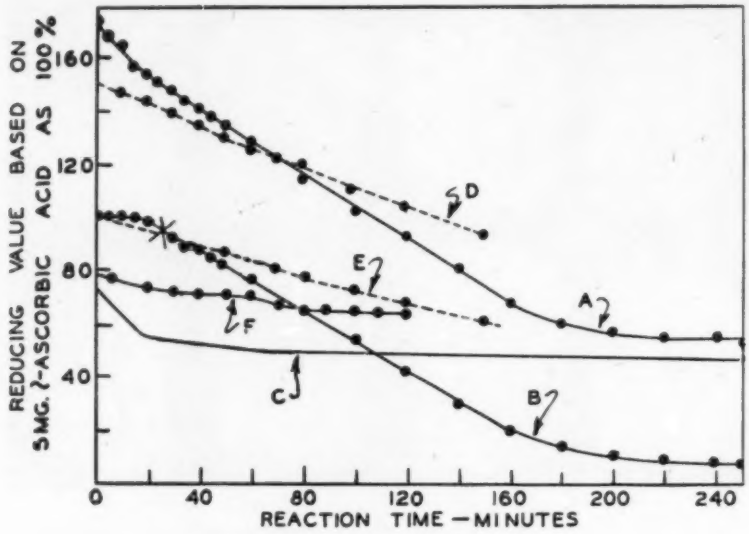


Fig. 7. Oxidation in second clear flour extracts.
Curve A—iodine titrations on unheated extract containing 5 mg % ascorbic acid.
Curve B—indophenol titrations on unheated extract containing 5 mg % ascorbic acid.
Curve C—difference between curves A and B.
Curve D—iodine titrations on boiled extract containing 5 mg % ascorbic acid.
Curve E—indophenol titrations on boiled extract containing 5 mg % ascorbic acid.
Curve F—iodine titrations on unheated extract containing no ascorbic acid.
X—indicates disappearance of nitroprusside reaction.

iodine titration curve (A) shows continuous oxidation during this time at a rate somewhat more rapid than the subsequent AA oxidation, indicating that during the period covered by the plateau in curve B the DHA (imperceptible during this period) was oxidizing some reducing groups at the same rate at which it (DHA) was being produced. The slightly greater rate of oxidation shown during this period may be accounted for by other oxidations as shown by curve F, the oxidation of a flour extract under the same conditions but without AA.

That a heat-labile enzyme system is involved in the AA oxidation is shown by comparable reactions carried out in boiled flour extracts

(curves D and E)—AA was quite rapidly oxidized in the boiled extract but more slowly than in the enzymatically active extract.[4]

There was no plateau at the beginning of the oxidation curve for the boiled extract, which could indicate that the reduction of DHA

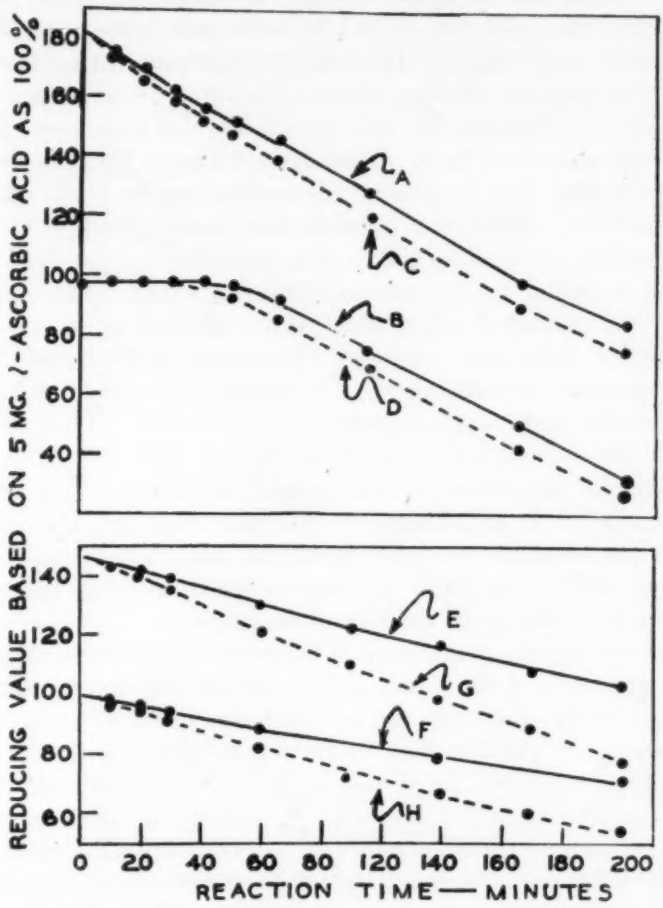


Fig. 8. The effect of light on oxidation in second clear flour extracts containing 5 mg % ascorbic acid. Curves A, B, E, and F show reaction rates in the absence of light; C, D, G, H in 200 ft. candles of light.

Curves A and C—iodine titrations on unheated extract.
Curves B and D—indophenol titrations on unheated extract.
Curves E and G—iodine titrations on boiled extract.
Curves F and H—indophenol titrations on boiled extract.

responsible for the plateau was enzymatically induced. However, this also may be attributed to the destruction during the boiling procedure of certain reducing compounds of the flour extract.

A peculiarity of the oxidation in boiled extracts is its acceleration by light. Figure 8 shows the oxidation of AA by unheated and by

[4] The pH of the boiled extract was 6.18 before and 6.05 after the addition of the AA.

boiled extracts in the absence of light and exposed (while being stirred in square pint Mason jars) to 200 foot-candles obtained from a 15 watt fluorescent light at a distance of 4½ inches. Mattick and Kon (1933) observed that vitamin C was destroyed in milk on exposure to diffused daylight. Kon and Watson (1936), investigating this reaction, showed that the oxidation of AA in milk was promoted by visible light of short wave length. Hopkins (1938) reported that lactoflavin (or its decomposition product, lumichrome) was the sensitizer for this photocatalytic oxidation and that lactoflavin did not cause oxidation of AA in the absence of light. Since from 0.3 μg to 2.0 μg of riboflavin per gram of flour may be present, depending on the grade (Andrews, Boyd, and Terry, 1942), it is possible that the acceleration by light is due to riboflavin and, accordingly, that there are two catalysts for AA oxidation in boiled flour extracts: riboflavin which is active only in the light and another catalyst which is not affected by light.

Sulfhydryl Oxidation. Borsook, Davenport, Jeffreys, and Warner (1937) tried various substances as reducing agents for DHA, but of those tried only sulfhydryl compounds were effective. They concluded that it would seem a safe generalization that only the -SH group is physiologically significant in this respect. However, their reactions were carried out in the absence of enzymes and, therefore, may not apply to physiological reactions involving enzyme systems. Warren (1943) has shown that other substances are oxidized in the presence of air and AA even in the absence of enzymes.

If the active reducing groups of flours are sulfhydryls, the time of the disappearance of the nitroprusside test for -SH should correspond to the end of the plateau in the AA oxidation curve (Figure 7). The nitroprusside end point in flour extracts is indistinct and only roughly approximate; however, in so far as could be determined, this test became negative at about the time corresponding to the end of the plateau—shown by the X on curve B. Accordingly, the value for AA oxidizable substance which may be obtained from the curves of Figure 7 may be tentatively considered a measure of sulfhydryl in the extract.

The nitroprusside test on the flour extract after boiling became faint—it was so nearly negative at the start that no satisfactory end point could be detected. This indicated loss of -SH on boiling probably accounts for part of the loss of reducing value—shown by the boiled extract curve (D) starting at 152%, whereas the original extract curve (A) started at 175%.

Oxidation of GSH in Flour Extracts. Further evidence for the hypothesis that the plateau was due to oxidation of a compound similar to GSH was obtained by studying the effect of GSH on ascorbic acid oxidation in flour extracts. Figure 9 shows the oxidation curves

obtained with the addition of 5 mg % GSH to unheated and to boiled extracts. In the unheated extract the AA plateau was extended 50 minutes, from 20 minutes (Figure 7) to 70 minutes (Figure 9), an amount corresponding to the time required to oxidize about 30% of the AA. Theoretically this is approximately the time expected; 5 mg of GSH has a reducing value equivalent to 1.43 mg AA which is 28.6% of 5 mg. As indicated by the disappearance of the nitro-

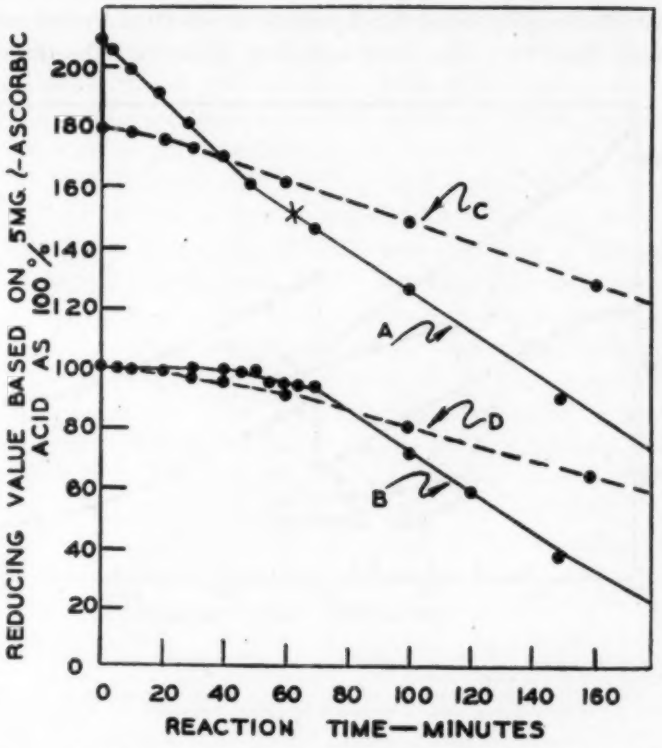


Fig. 9. Oxidation in unheated second clear flour extracts containing 5 mg % glutathione and 5 mg % ascorbic acid.
Curve A—iodine titrations on unboiled extract.
Curve B—indophenol titrations on unboiled extract.
Curve C—iodine titrations on boiled extract.
Curve D—indophenol titrations on boiled extract.
X—indicates disappearance of nitroprusside reaction.

prusside test (X on curve A), the end of the plateau corresponds approximately to the disappearance of -SH groups.

The addition of GSH to the boiled extract at the beginning of the reaction had little effect; the rate of oxidation of AA and of flour reducing matter (including the GSH) as evinced by curves C and D was similar to that in a boiled extract without GSH (curves D and E of Figure 7). The presence of GSH did not produce a plateau in the

AA curve (D), indicating that the reduction of DHA which caused the plateau in the unheated extracts was enzymatically induced.

Dehydroascorbic Acid as an Oxidizing Agent in Flour Extracts

The oxidation of GSH by DHA in flour extracts is exceedingly rapid. Curves A and B of Figure 10 show the effect of the addition of 5 mg % GSH to the flour extract after about 60% of the AA had been enzymatically oxidized to DHA. The jump in the iodine titration curve on the addition of GSH merely shows that a reducing agent was added; however, the corresponding jump in the indophenol

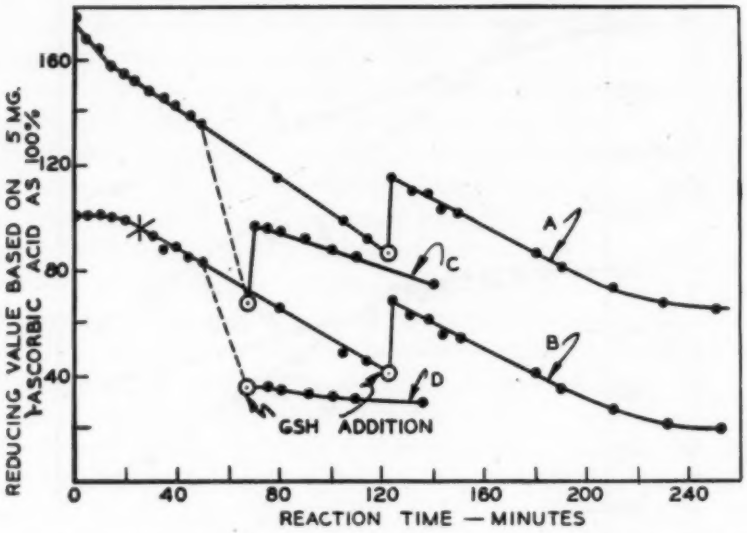


Fig. 10. Oxidation of 5 mg % GSH by oxidized ascorbic acid in heated and unheated flour extracts.
Curves A and B—unheated extract.
Curves C and D—boiled extract; dotted lines indicate period of heating and recooling.
Curves A and C—reducing value determined by iodine titration.
Curves B and D—ascorbic acid determined by indophenol.
X—disappearance of -SH test.

titration curve shows that the GSH rapidly reduced DHA to AA. The reduction of DHA, increase in AA from 40% to 68% (curve B), was equivalent to the 5 mg % of GSH added. The reaction was complete within the one minute interval required for introducing the GSH and taking the aliquots for the determinations. The nitroprusside test also became negative during this time.

The contrast between this rapid oxidation of GSH and the relatively slow oxidation of *doughs* by DHA (Figure 6) is an indication that at least a part of the material responsible for the reduced character of unoxidized doughs is considerably more difficult to oxidize than GSH.

That the rapid oxidation of GSH by DHA is enzymatically induced

may be inferred by comparison with the slow oxidation in nonenzymatic solutions as shown by Borsook *et al* (1937) and from the work reported by Hopkins and Morgan (1936), Crook and Hopkins (1938), Crook (1941), and Crook and Morgan (1944), showing that the oxidation of GSH by DHA in plant juices is promoted by enzyme action. Presumably this could be shown in flour extracts by adding GSH to a flour extract which has been boiled after enzymatic production of DHA.

Curves C and D of Figure 10 were obtained by heating a flour extract originally containing 5 mg % AA after 18% of the AA had been oxidized. Rapid AA oxidation took place during the heating, supposedly before the oxidase was inactivated, decreasing the AA to 36%. The dotted portions of curves C and D represent the period of heating and recooling to 30°C. Five mg % of GSH was then added as shown. As indicated by the absence of a jump in curve D, the exceedingly rapid oxidation of GSH which occurs in enzymatically active extracts (jump in curve B) did not take place but was replaced by a plateau with oxidation of GSH (shown by the decline of curve C) taking place at a rate similar to that of AA oxidation in boiled extracts; compare the rate shown in curve C after the GSH addition with that in curves D or E of Figure 7. The plateau of curve D shows that the DHA produced before and during the heating process was unable to oxidize GSH but that the newly formed DHA was oxidizing GSH as rapidly as it (DHA) was being formed. This could indicate that the DHA had been converted to the nonoxidizing diketogulonic acid while the enzymes were being inactivated by heat. A determination of DHA by the H_2S method indicated that only 12% of the DHA which was supposedly present was actually in the solution. Since Penney and Zilva (1943) found that the H_2S method is not absolutely reliable, it might be inferred that the DHA had been completely converted to diketogulonic acid. Accordingly, in order to show whether an enzyme is present in flour which utilizes DHA for oxidation of -SH, chemically produced DHA was added to flour extracts.

Dehydroascorbic acid prepared by iodine oxidation of AA in absolute alcohol (Hirst method) may be 75% reduced to AA by H_2S. Accordingly, 3.3 mg % (equivalent to 2.5 mg % of pure DHA) was added both to unheated and to boiled extracts (boiled and cooled before the addition of DHA). Sufficient time was allowed to establish the slope of the curve for the oxidation of flour reducing substances and then 5 mg % GSH was added. The data obtained using a second clear flour extract are given in Figure 11.

On the addition of DHA to the unheated extract (curve A) there was a rapid loss of reducing value of the flour extract equivalent to

0.25 mg % of AA. At present we believe this to be due tc a direct combination of DHA with some reducing component of wheat germ. This reaction is less noticeable in first clear extracts, amounting to approximately 0.1 mg % of AA, and is imperceptible in patent flour extracts. It may be obtained in extracts of a mixture of 5% finely ground germ in patent flour. This reaction does not occur on the addition of DHA to boiled extracts (curve C).

The rate of oxidation of flour reducing substances in the enzymatically active flour extract was increased by the addition of DHA

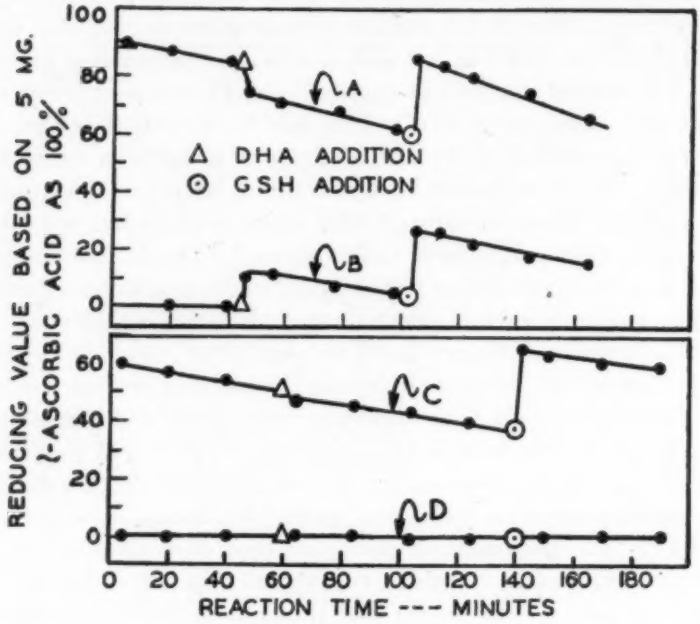


Fig. 11. Oxidation with dehydroascorbic acid in flour extracts.
Curves A and B—unheated extract.
Curves C and D—boiled extract.
Curves A and C—iodine titrations.
Curves B and D—indophenol titrations.

(compare the slope of curve A before and after the addition of DHA), whereas there was no apparent change in the rate of oxidation in the boiled extract on the addition of DHA (curve C). That some substance in the flour extract was quite rapidly oxidized by the DHA is emphasized by the reduction which occurred in the DHA (curve B immediately after the DHA addition). No such reduction of DHA took place in the boiled extract (curve D).

The oxidation of added GSH by the DHA in the enzymatically active extract was complete in the minute required for mixing and taking the aliquot for analysis (curve B jump in AA on addition of

GSH). On the other hand, no reduction of DHA could be detected in the inactivated extract (curve D). This indicates that an enzyme which was destroyed by boiling was necessary for the oxidation of GSH by DHA under these conditions.

The rate of oxidation as indicated by the slight decline in curve C of Figure 11, after the jump due to the GSH addition, is similar to the rate of oxidation shown for the flour reducing substances before the GSH addition; indicating that the added GSH was not necessarily the substance which was being oxidized. However, curves C and D of Figure 10 indicate oxidation of GSH but only as fast as DHA was being formed.

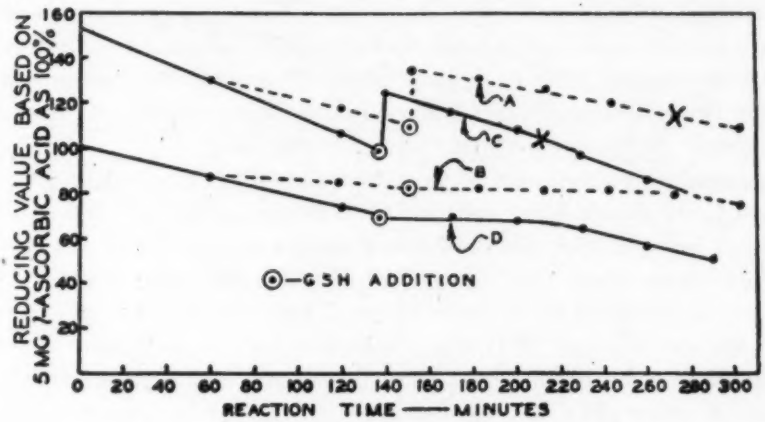


Fig. 12. The effect of active ascorbic acid oxidation on the rate of -SH oxidation in boiled flour extracts.
Curves A and B show reaction rates in the absence of light; curves C and D in 200 ft. candles of light.
X—indicates disappearance of nitroprusside reaction.
Curves A and C—iodine titrations.
Curves B and D—indophenol titrations.

Since the rate of AA oxidation in boiled extracts may be varied by changes in light intensity, this offers a possibility for further confirmation of the effect of *active* AA oxidation on the oxidation of GSH. Five mg % of AA was added to a boiled extract and DHA produced by air oxidation in 200 foot-candles of light. When 14% of the AA had been oxidized, the solution was divided—half remaining in the light and the other half being placed in the dark. The oxidation was allowed to proceed for about 80 minutes longer to establish the slope of the curves.[5] Glutathione was added as indicated in Figure 12. As shown by curves B and D, after the addition of GSH there was no perceptible reduction of the DHA and no perceptible oxidation of AA, indicating that the DHA which was available was not rapidly reduced

[5] About 75% of the DHA thus obtained, whether in the light or in darkness, could be recovered as AA by H_2S treatment.

by GSH. However, after the jump in the iodine titration curves A and C (which merely show the presence of the added GSH or its equivalent in reducing value), the curves indicate oxidation rates similar to the rates which they show before the GSH addition; curve A shows oxidation at the rate of approximately 0.5 mg % (AA equivalent) per hour both before and after the GSH addition, whereas curve C shows oxidation at a rate of about 1.0 mg % per hour before and after the GSH addition. Since, according to the indophenol curves B and D, each of the iodine titration curves includes oxidation of AA before but not after the GSH additions, the rate of oxidation of GSH was the same as the rate of oxidation of AA. Obviously, the DHA, which had accumulated previous to the GSH addition, had no effect on the rate of oxidation of GSH and seemingly only the freshly formed DHA was readily able to oxidize GSH—that which had accumulated before the addition of GSH was relatively inactive (except, as shown previously, in the presence of the active enzyme).

According to the rates of oxidation shown in curves A and C, the added GSH should have been oxidized at approximately 280 and 220 minutes respectively; the plateaus of curves B and D end at approximately these respective times and the nitroprusside reaction also became negative at about these times. This is considered as evidence that the oxidation of GSH was responsible for the plateaus.

It should be emphasized that the above observations may not apply at other pH's, and do not apply in case greater concentrations of GSH are used. In the absence of enzymes Borsook *et al* (1937) found that the degree of reduction of DHA at any given pH and temperature was dependent mainly on the concentration of GSH; 200 mg % GSH acting on 4 mg % DHA at pH 7 and 37.5°C gave 96% reduction, 20 mg % GSH gave 13%, and 4 mg % only 3% reduction in a 4-hour period of time.

Variations between Flours in Ascorbic Acid Oxidase Activity. Extracts from different flours, different grades from one mill mix or the same grade from different mills, vary considerably in the rate at which they oxidize AA. This is illustrated in Figure 13 which shows reaction curves for three grades of flour from one mill mix (flours No. 4) and for a first clear from another mill (No. 2). The reaction curves for the second clear flour No. 4 also may be compared with those of the second clear No. 1 shown in Figure 7.

Oxidation was slow in the 85% patent flour extract, more rapid in the first clear extracts, and still more rapid in the second clear extracts. Whereas the first clear flour No. 4 differed markedly from the first clear No. 2 in the quantity of oxidizable material (compare curves of

Figure 13), the rate of oxidation of AA was quite similar in the two. This also was true of the second clear No. 4 in comparison with the second clear No. 1 shown in Figure 7.

Oxidation in Boiled Extracts. Apparently the catalyst which promoted the oxidation in boiled extracts varied, as did the heat-labile enzyme, with the flour grade. That this heat-stable catalyst may be of considerable importance may be judged from the relative

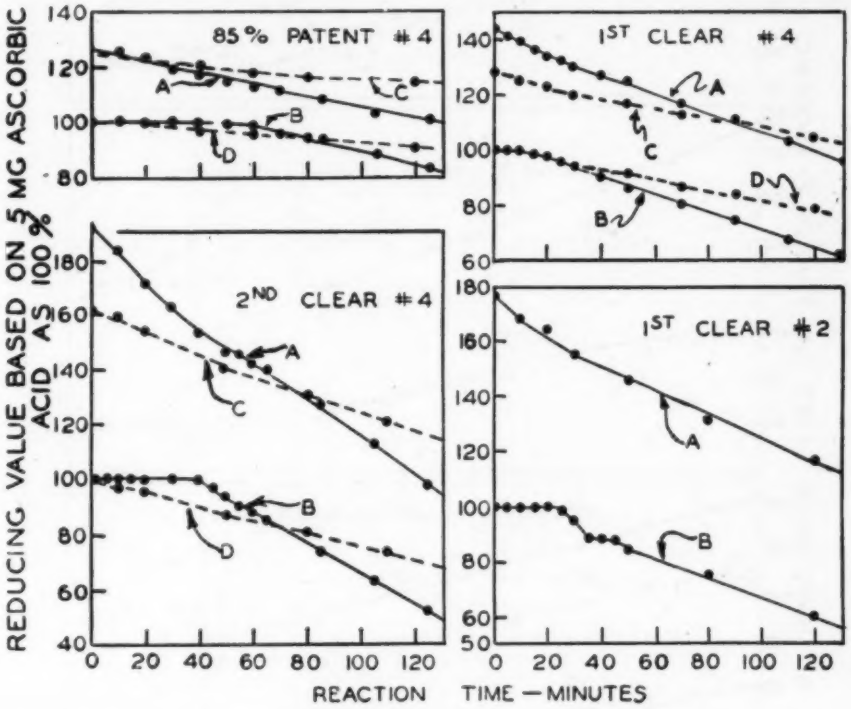


Fig. 13. Variations in oxidation between flour extracts.
Curves A and B—unheated extract.
Curves D and C—boiled extract.
Curves A and C—iodine titrations.
Curves B and D—indophenol titrations.

amount of oxidation induced by this factor as compared with that induced by the heat-labile enzyme.

Reducing Matter Not Oxidizable by the Dehydroascorbic Acid-Reductase System. The data presented in Figure 13 show that there were marked differences between flour extracts in the amount of reducing matter which was oxidizable by iodine but not by the ascorbic acid-enzyme system; these differences may be estimated by comparing the distances between the AA curves and the corresponding iodine titration curves for the respective flours. In clear flour extracts,

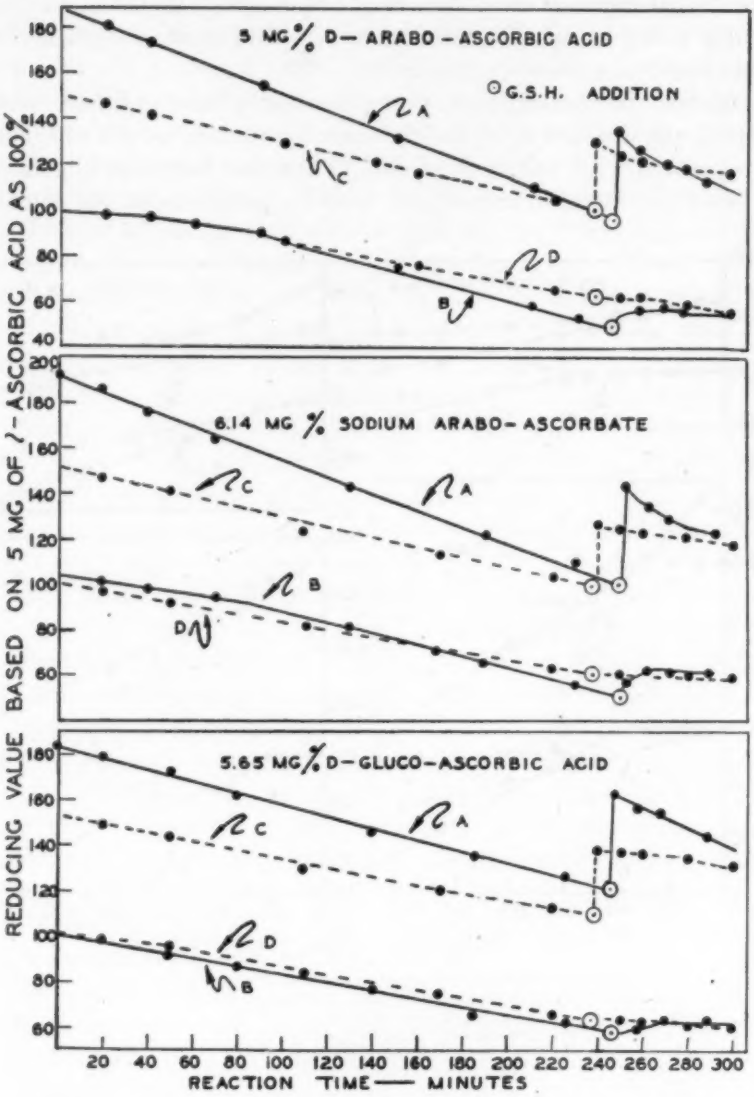


Fig. 14. Oxidation in second clear flour extracts containing analogs of ascorbic acid.
Curves A and B—unheated extract.
Curves C and D—boiled extract.
Curves A and C—iodine titrations.
Curves B and D—indophenol titrations.

appreciable amounts of this material disappeared on boiling, whereas there was little loss from the patent flour extract (curves A and C for each flour); this corresponds to the loss of protein (by coagulation) from these respective extracts on boiling.

The Reaction of Ascorbic Acid Analogs in Flour Extracts

Oxidation. Since the ascorbic acid analogs were found to be less effective than AA as oxidizing agents in doughs, it was of interest to compare their reactions in flour extracts. The analogs and reductone (in quantities equivalent, on a molecular basis, to 5 mg % of AA) were added to both boiled and unheated extracts. The reaction curves shown in Figures 14 and 15 are for reactions carried out in the dark. For each reaction study, 5 mg % of GSH was added as shown. The rates of oxidation shown in these curves may be compared with those for AA (in the dark) shown in Figure 8.

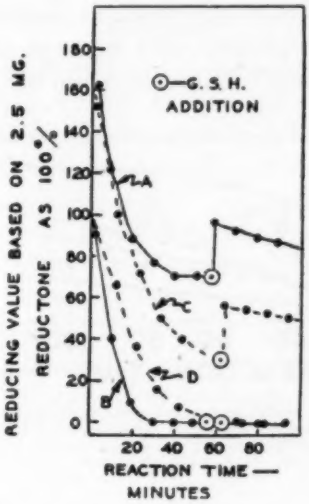


Fig. 15. Oxidation in second clear flour extracts containing reductone.
Curves A and B—unheated extract.
Curves C and D—boiled extract.
Curves A and C—iodine titrations.
Curves B and D—indophenol titrations.

The oxidation of the analogs in unheated extracts was much slower than the oxidation of AA, whereas the oxidation of reductone was exceedingly rapid (Figure 15).

A comparison of the rates of oxidation in unheated extracts with those in boiled extracts shows that the heat-labile ascorbic acid oxidase of flour extract had only slight action on the analogs; the oxidations were almost as rapid in the boiled extracts as in the unboiled. The rate of oxidation actuated by the heat-stable catalyst was essentially the same on all of the ascorbic acids, including AA. On the other hand, reductone was much more rapidly oxidized in both boiled and unboiled extracts.

The data given in Figures 14 and 15 in conjunction with the baking

data indicate that the comparative rates of oxidation of compounds related to AA are not dependable as indications of their value as oxidizing agents in doughs; reductone was rapidly oxidized but seemingly acted as a reducing agent in doughs.

Oxidation of GSH. The ability of the oxidized analogs and of oxidized reductone to take part in the enzymatically induced oxidation of GSH may be inferred from that portion of the curves, shown in Figures 14 and 15, after the addition of GSH. That the oxidized analogs and reductone were quite ineffective in the oxidation of GSH is indicated by the small amount of reduction which took place on the addition of GSH (curve B for each).

The slight reduction of the oxidized analogs by GSH might be considered as an indication that they were not present as the reducible dehydro-type compounds. However, from 65% to 75% of the theo-

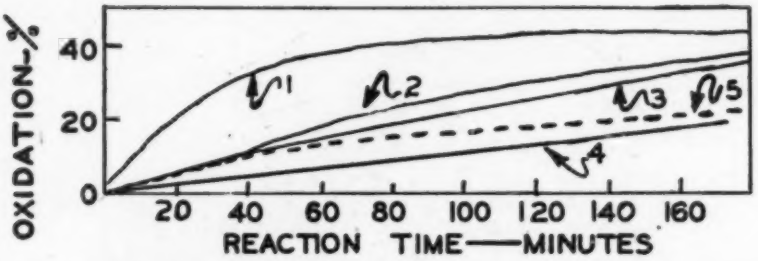


Fig. 16. Comparison of the oxidation brought about in flour extracts by the addition of *l*-ascorbic acid or of its analogs. Oxidation in percent of total reducing material oxidizable by iodine. (1) *l*-ascorbic acid; (2) *d*-arabo-ascorbic acid; (3) *d*-arabo-ascorbate; (4) *d*-gluco-ascorbic acid; (5) flour extract only.

retical quantity of the dehydrocompounds could be recovered as the reduced compounds by treatment with H_2S. Accordingly, this slight oxidation of GSH indicates that the dehydroascorbic acid reductase of flour was quite limited in its ability to utilize these analogs of DHA.

Considering the relative ineffectiveness of these compounds as oxidizing agents in doughs, the absence of a plateau at the beginning of the indophenol curves is noteworthy. The slower rate of oxidation of *d*-arabo-ascorbic acid during, approximately, the first 80 minutes (curve B) may be significant since this analog had some oxidizing action in doughs, whereas *d*-gluco-ascorbic acid had none. The iodine titration curve (A) for *d*-arabo-ascorbic acid shows a more rapid oxidation of flour reducing matter than is shown by the curve for *d*-gluco. Hence it was of interest to calculate from these data the oxidation which took place in each extract. The curves thus obtained are given in Figure 16. Curve 5 for the oxidation in flour extract with no added reagent is given for comparative purposes.

It is apparent that the rate of oxidation induced by the analogs in flour extract is in agreement with the oxidation which they effected in doughs. *d*-Gluco-ascorbic acid depressed the oxidation below that which occurred in the absence of reagent. Oxidation of reductone was so rapid that considerable error was involved in the determination of oxidation at a specified time. Also, as pointed out by Snow and Zilva (1938), its oxidation is complicated by side reactions. However, even though questionable, the calculation of oxidation in the presence of reductone indicated that reductone had no oxidizing effect on doughs—the oxidation curve seems to be similar to the curve for flour extract with no added reagent (curve 5).

Summary

The ascorbic acid analogs which were used in this study (*d*-gluco-ascorbic and *d*-arabo-ascorbic acids) were quite ineffective as oxidizing agents in doughs. The oxidized analogs were somewhat more effective but not as effective as dehydro-*l*-ascorbic acid. Reductone, reduced or oxidized, had no oxidizing action. Accordingly, the presence of "an enediol group next to a carbonyl group in a compound" is no assurance that the compound will act as a chemical flour improver.

Oxidation of ascorbic acid in flour extracts was effected by a heat-labile enzyme similar to that reported in other plant extracts. However, a heat-stable catalyst which was quite effective in the oxidation was found to be present also. The heat-stable factor was not inactivated by glutathione.

The activity of both the heat-labile and heat-stable factors varied with the flour grade.

Oxidation in boiled extracts was affected by light intensity, indicating that, in the presence of light, riboflavin may be a third factor promoting oxidation of ascorbic acid in flour extracts.

The ascorbic acid oxidase-dehydroascorbic acid reductase enzyme system present in flour extract was found to be quite similar to that described by Hopkins, Morgan, and Crook for other plant extracts.

The evidence indicates that the dehydroascorbic acid reductase system oxidizes -SH groups of the flour extract. There is a considerable quantity of reducing material in flour extract which is oxidizable by means of iodine but not by dehydroascorbic acid.

In the concentrations and at the pH's used in this investigation, preformed dehydroascorbic acid was unable to oxidize glutathione except in the presence of dehydroascorbic acid reductase. However, oxidation of glutathione did take place in boiled extracts in the presence of active ascorbic acid oxidation.

The ascorbic acid oxidase of flour had little action on the analogs

of ascorbic acid. On the other hand, the heat-stable catalyst effected the oxidation of the analogs and *l*-ascorbic acid at essentially the same rate.

The dehydroascorbic acid reductase–sulfhydryl system was unable effectively to reduce the oxidized analogs.

The comparative oxidizing actions of ascorbic acid and its analogs may be explained by their relative ability or inability to take part in the enzymatically induced oxidation of certain reducing groups which are present in flour.

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MULTIPLE BLEACHING OF FLOUR. II. BLEACHING EFFICIENCY IN SYSTEMS INVOLVING NITROGEN PEROXIDE AND ANOTHER BLEACHING GAS[1]

W. S. HUTCHINSON, C. G. FERRARI,[2] and R. I. DERBY

General Mills, Inc., Minneapolis, Minnesota

(Presented at the Annual Meeting, May 1944; received for publication July 17, 1944)

The purpose of the experiments reported in this paper was to ascertain the most efficient way to utilize nitrogen peroxide in combination with another gaseous bleaching agent in the multiple bleaching of flour. Nitrogen peroxide is of importance in flour bleaching because of its cheapness and the fact that it has little or no effect on the baking properties of flours.

In the first paper in this series, multiple bleaching was defined as the treatment of flour with repeated small dosages of a single gaseous bleaching agent. In the present study, the definition is expanded to include the bleaching of flour with two or more gases added either simultaneously or in sequence.

The results obtained by bleaching on experimental batch, pilot, and commercial scale equipment were described in the first paper in this series by Ferrari, Hutchinson, and Mecham (1944). The commercial

[1] Paper No. 55, Journal Series, General Mills, Inc., Research Laboratories.
[2] Present address: Standard Brands, Inc., New York.

system was the least efficient in terms of color removal. Among other things, it was shown that two horizontal-type commercial agitators in series were no better than one when a single gaseous bleaching agent was applied to the first agitator. However, when the gaseous agent was distributed between two agitators, preferably equally, better color removal was achieved. Multiple bleaching consisting of treating flour with repeated small dosages of a single reagent effected better color removal than the same dosage applied as a single treatment.

Apparatus and Procedures

The experimental procedures and equipment are described in the previous paper. Chlorine dioxide for flour bleaching purposes may be produced by the method of Hutchinson and Mecham (1943). Flour color is expressed as "carotene," according to the conventional procedure described by Binnington, Hutchinson, and Ferrari (1941). As related therein, the flours were extracted with water-saturated butyl alcohol, the extracts being read in an Evelyn photoelectric colorimeter with a 440-mμ filter. The "carotene" results were converted to the more customary naphtha alcohol basis by the equation shown in the first paper of this series.

Experimental

Simultaneous Treatment of Flour with Nitrogen Peroxide and Nitrogen Trichloride. When two gaseous reagents, such as nitrogen peroxide and nitrogen trichloride, were applied to a flour simultaneously by introducing them both into the same agitator, there appeared to be an interaction which deprived them of fully independent activity, and hence the color removal expected was not secured. In Table I the

TABLE I

NITROGEN PEROXIDE AND NITROGEN TRICHLORIDE APPLIED SIMULTANEOUSLY TO A PATENT FLOUR IN A COMMERCIAL MILL

Bleaching treatment				"Carotene"	Color removal
Nitrogen trichloride		Nitrogen peroxide			
Amount	Applied to agitator No.	Amount	Applied to agitator No.		
g/bbl		*g/bbl*		*ppm*	%
2	2	0.8	2	1.22	45
2	2	—	—	1.22	45
—	—	0.8	1	1.60	29
			Unbleached flour	2.24	—

results of such an experiment are given. The experimental equipment in a commercial mill was arranged with two flour agitators connected in series. When 2 g nitrogen trichloride and 0.8 g nitrogen peroxide (per bbl of flour) were applied simultaneously in agitator No. 2 (the second), the "carotene" value obtained was 1.22 ppm, corresponding to a color removal of 45%. It will be seen from the data that 2 g nitrogen trichloride alone, without any nitrogen peroxide, reduced the "carotene" value as much as the combination, making it appear that no practical benefit can be expected from the simultaneous application of these two reagents. Eight-tenths g nitrogen peroxide alone lowered the "carotene" value 29%, a rather substantial reduction in pigmentation. This type of result has been obtained frequently, and the theory of the authors is that there is probably some interaction between the gaseous reagents which causes a loss of efficiency. No chemical proof has been sought.

Multiple Bleaching of Flour Using Nitrogen Peroxide and Nitrogen Trichloride Simultaneously or Sequentially. A comparison of the simultaneous and sequential application of nitrogen peroxide and nitrogen trichloride to flour is given in Table II. A treatment with

TABLE II

NITROGEN TRICHLORIDE AND NITROGEN PEROXIDE APPLIED TO A PATENT FLOUR SIMULTANEOUSLY OR SEQUENTIALLY

Bleaching treatment per bbl of flour	"Carotene"
	ppm
Simultaneous: 2 g NCl_3 and 1.5 g NO_2	0.98
Sequential: 1.5 g NO_2 followed by 2 g NCl_3	0.92
Sequential: 2 g NCl_3 followed by 1.5 g NO_2	0.78
2 g NCl_3 and 0.048 oz benzoyl peroxide	0.66
Unbleached patent flour	2.20

2 g nitrogen trichloride and 0.048 oz benzoyl peroxide per bbl of flour substantially reduced the "carotene" value to 0.66 ppm, which is lower than the majority of commercially bleached patent flours. Two g nitrogen trichloride and 1.5 g nitrogen peroxide, applied simultaneously, reduced the "carotene" value to 0.98. When the gaseous reagents were applied sequentially, it was found that 1.5 g nitrogen peroxide applied first, followed by 2 g nitrogen trichloride, reduced the "carotene" to 0.92. However, when the reagents were applied in the opposite order, the "carotene" value was substantially lower, 0.78 ppm. Thus a preferred order of application in multiple bleaching is clearly apparent. As this type of result was interesting and had commercial implications of importance, an extensive series of experi-

ments was run to elucidate further this subject. Typical results will be described. U. S. Patents 2,324,203 and 2,351,809 to Ferrari and Hutchinson (1943 and 1944) cover some of these multiple bleaching treatments.

Multiple Bleaching with Nitrogen Peroxide and Nitrogen Trichloride. The effects of the order of application of nitrogen trichloride and nitrogen peroxide in two horizontal agitators connected in series in a commercial mill are shown for four flours in Table III.

Flour C will be selected for discussion because the data recorded cover a greater range of bleaching treatment, and the "carotene" value of the unbleached flour (3.18 ppm) is rather high. When the bleaching treatment comprised 2 g nitrogen trichloride and 0.75 g nitrogen peroxide per bbl of flour, the "carotene" value was 1.29 ppm when nitrogen trichloride was applied first, and 1.60 when nitrogen peroxide was applied first. Similarly, when the bleaching treatment consisted of 2 g Agene and 1.5 g nitrogen peroxide applied in the two ways, the "carotene" value was 1.07 ppm when nitrogen trichloride was applied first and 1.56 when nitrogen peroxide was applied first. All the data in the table substantiate the fact that greater color removal is always achieved when the nitrogen peroxide treatment follows the nitrogen trichloride. This has been exhaustively confirmed by the authors with three types of bleaching equipment and by research covering a period of several crop years.

A study of Table III will reveal other interesting facts. For example, it will be seen in some cases that the larger amount of nitrogen peroxide does not cause much more color removal than the smaller. In the first paper of this series it was noted that diminishing returns were soon encountered when the amount of nitrogen peroxide applied alone was increased beyond a certain point. For the sake of comparison, the color removal obtained by nitrogen trichloride alone is given in Table III for each flour. It will be noted that sometimes nitrogen trichloride alone will remove as much "carotene" as nitrogen peroxide followed by nitrogen trichloride—the less efficient order of application. As nitrogen peroxide is generally regarded as a milder, less efficient flour bleaching agent than many others, it is surprising that it is most efficiently used following a treatment with nitrogen trichloride which has stronger flour bleaching properties. These results, and the many others which the authors plan to describe, confirm the writers in the opinion that most of the flour bleaching agents act in a somewhat different way in spite of the fact that they are all oxidizing agents and decolorize carotinoid pigments. Gaseous bleaching agents have different oxidizing potentials and different chemical affinities for the various complex constituents of flour, a circumstance

TABLE III

FLOUR BLEACHING EFFICIENCY AS AFFECTED BY THE ORDER OF APPLICATION IN MULTIPLE BLEACHING TREATMENTS WITH NITROGEN PEROXIDE AND NITROGEN TRICHLORIDE IN TWO HORIZONTAL AGITATORS IN SERIES IN A COMMERCIAL MILL

Bleaching treatment per bbl of flour	"Carotene"
	ppm
Flour A	
Unbleached	2.43
2 g of NCl_3 alone	1.30
2 g NCl_3 followed by 0.75 g NO_2	1.10
0.75 g NO_2 followed by 2 g NCl_3	1.22
2 g NCl_3 followed by 1.5 g NO_2	1.07
1.5 g NO_2 followed by 2 g NCl_3	1.29
Flour B	
Unbleached	2.25
2 g NCl_3 alone	1.18
2 g NCl_3 followed by 0.75 g NO_2	0.93
0.75 g NO_2 followed by 2 g NCl_3	1.18
2 g NCl_3 followed by 1.5 g NO_2	0.97
1.5 g NO_2 followed by 2 g NCl_3	1.21
Flour C	
Unbleached	3.18
2 g NCl_3 alone	1.65
3 g NCl_3 alone	1.12
2 g NCl_3 followed by 0.75 g NO_2	1.29
0.75 g NO_2 followed by 2 g NCl_3	1.60
2 g NCl_3 followed by 1.5 g NO_2	1.07
1.5 g NO_2 followed by 2 g NCl_3	1.56
3 g NCl_3 followed by 0.75 g NO_2	1.07
0.75 g NO_2 followed by 3 g NCl_3	1.20
3 g NCl_3 followed by 1.5 g NO_2	0.98
1.5 g NO_2 followed by 3 g NCl_3	1.29
Flour D	
Unbleached	2.49
2 g NCl_3 alone	1.20
2 g NCl_3 followed by 0.75 g NO_2	0.96
0.75 g NO_2 followed by 2 g NCl_3	1.07

causing them, in some cases, to react preferentially with constituents other than carotinoid pigments. Thus, some may react with non-carotinoid molecules prior to their attack on "carotene" itself, or at least the rates of reaction between the bleaching agent and the substances with which it reacts may well be different with different bleaching agents.

When bleaching was carried out with nitrogen trichloride and nitrogen peroxide in the preferred order (nitrogen trichloride followed by nitrogen peroxide), and the partial pressure of the nitrogen trichloride was varied over the range possible with present commercial equipment, the results shown in Table IV were obtained. Supplements of benzoyl peroxide were also added to measure the increased color removal effected by dosages from 0.016 to 0.048 oz/bbl of flour. At all levels of nitrogen peroxide used, namely, 0.8, 1.5, and 1.9 g/bbl of flour, the higher partial pressures of nitrogen trichloride tended to give better results when no benzoyl peroxide was added subsequently. The same trend was true when the smallest dosage (0.016 oz/bbl) of

TABLE IV

EFFECT OF PARTIAL PRESSURE OF NITROGEN TRICHLORIDE UPON COLOR REMOVAL OF PATENT FLOUR BLEACHED WITH NITROGEN TRICHLORIDE FOLLOWED BY NITROGEN PEROXIDE

Nitrogen trichloride		Nitrogen peroxide	"Carotene" with stated amounts of benzoyl peroxide added			
Agitator 1	Partial pressure	Agitator 2	None	0.016 oz/bbl	0.032 oz/bbl	0.048 oz/bbl
g/bbl	*mm Hg*	*g/bbl*	*ppm*	*ppm*	*ppm*	*ppm*
2	0.50	0.8	0.95	0.90	0.75	—
2	1.15	0.8	0.93	0.88	0.77	—
2	1.50	0.8	0.87	—	0.75	0.69
2	0.50	1.5	0.95	0.78	0.71	—
2	1.15	1.5	0.97	0.78	0.75	—
2	1.50	1.5	0.88	—	0.76	0.72
2	0.50	1.9	0.87	0.83	0.72	—
2	1.15	1.9	0.97	0.78	0.72	—
2	1.50	1.9	0.86	—	0.75	0.75

benzoyl peroxide was added. At higher dosages (0.032 and 0.048 oz/bbl) of benzoyl peroxide, the final "carotene" value was not decreased when higher partial pressures of nitrogen trichloride were employed. In these instances there were probably sufficient total bleaching reagents added to mask the effects of the nitrogen trichloride partial pressures on the resultant color removals. All of the "carotene" is not removed with equal ease; and it is an established fact that as the "carotene" level decreases, the residual quantity is more and more difficult to remove, requiring relatively more bleaching agent to accomplish a fixed increment of color removal. This is true of all bleaching agents studied.

Multiple Bleaching with Nitrogen Peroxide and Hypochlorous Acid. The order of application of nitrogen peroxide and hypochlorous acid

likewise influenced color removal. Experimental data for two patent flours and one first clear flour are given in Table V. Nitrogen trichloride with benzoyl peroxide was included for purposes of comparison, since it simulated commercial practice at that time. In the case of patent flour No. 1, the treatments per bbl of flour consisted of 1.5 g nitrogen peroxide followed by 25 g hypochlorous acid and the reverse order of application. The "carotene" value of the former was 1.13 ppm, of the latter 0.84 ppm, a substantial difference. Patent flour No. 2 was treated with 1.5 g nitrogen peroxide and 20 g hypochlorous acid per bbl. The preferred order of application was again the same, as can be seen by a comparison of the "carotene" values 1.11 and 0.93 ppm. A first clear flour will be found in Table V by

TABLE V

MULTIPLE BLEACHING WITH NITROGEN PEROXIDE AND HYPOCHLOROUS ACID IN BATCH SCALE EQUIPMENT. EFFECT OF ORDER OF APPLICATION ON COLOR REMOVAL

Bleaching treatment per bbl flour	pH of flour	"Carotene"
		ppm
Unbleached patent flour No. 1	5.80	2.48
2 g NCl_3 plus 0.048 oz benzoyl peroxide	5.78	0.67
1.5 g NO_2 followed by 25 g HOCl	5.64	1.13
25 g HOCl followed by 1.5 g NO_2	5.71	0.84
Unbleached patent flour No. 2	5.86	2.41
2 g NCl_3 plus 0.048 oz benzoyl peroxide	5.84	0.70
1.5 g NO_2 followed by 20 g HOCl	5.68	1.11
20 g HOCl followed by 1.5 g NO_2	5.76	0.93
Unbleached first clear flour	6.18	2.91
5 g NCl_3	6.14	1.20
1.5 g NO_2 followed by 25 g HOCl	6.15	1.44
25 g HOCl followed by 1.5 g NO_2	6.10	1.27

way of example to show that the preferred order of application, namely, hypochlorous acid followed by nitrogen peroxide, applies to this type of flour as well as to a patent flour. A further point of interest is the fact that 25 g hypochlorous acid followed by 1.5 g nitrogen peroxide gave a "carotene" value of 1.27 ppm, as compared with 1.20 ppm achieved by 5 g nitrogen trichloride. The pH of the flour samples was measured. There is a tendency toward a slightly lower pH value in all of the samples bleached with hypochlorous acid and nitrogen peroxide as compared with nitrogen trichloride. The order of application does not affect pH to a marked degree, although in the case of the patent flours the preferred order of application for color removal (hypochlorous acid followed by nitrogen trichloride) appeared to give a slight but uniformly higher pH value.

Multiple Bleaching with Chlorine Dioxide and Nitrogen Peroxide. In considering chlorine dioxide and nitrogen peroxide combinations, comparisons of their simultaneous and sequential application to flour were made. Typical results are shown in Table VI. With these

TABLE VI

CHLORINE DIOXIDE AND NITROGEN PEROXIDE APPLIED TO A PATENT FLOUR SIMULTANEOUSLY OR SEQUENTIALLY IN MULTIPLE BLEACHING

Bleaching treatment per bbl of flour	"Carotene"
	ppm
Unbleached patent flour	2.20
2 g NCl_3 plus 0.048 oz benzoyl peroxide	0.66
Simultaneous: 0.8 g ClO_2 and 1.5 g NO_2	1.05
Sequential: 1.5 g NO_2 followed by 0.8 g ClO_2	0.96
Sequential: 0.8 g ClO_2 followed by 1.5 g NO_2	0.88

reagents, sequential application in any order achieved more color removal than simultaneous application. Here, too, one reagent appeared to interfere or react with the other, reducing bleaching efficiency. The preferred order of application always was chlorine dioxide followed by nitrogen peroxide. Thus 1.5 g nitrogen peroxide followed by 0.8 g chlorine dioxide gave a "carotene" value of 0.96 ppm. The reverse order resulted in a "carotene" value of 0.88 ppm. When the "carotene" values are of this order of magnitude, the difference between those cited above is substantial. Simultaneous application of the two reagents in the above amounts gave a "carotene" value of 1.05 ppm—a substantially poorer bleach than either sequence produced. Bleaching with 2 g nitrogen trichloride and 0.048 g benzoyl peroxide was placed in the table for purposes of comparison. In this instance the color removal with these reagents ("carotene" value 0.66 ppm) was greater than in the majority of commercially bleached flours.

The data of another study of chlorine dioxide and nitrogen peroxide have been included in Table VII. Here, the data are more extensive than the preceding. Three different levels of chlorine dioxide were employed, namely, 0.8, 1.1, and 1.4 g/bbl of flour. This reagent has a more powerful bleaching action per gram than any of the others, and the difference of 0.3 g/bbl in the dosage levels is substantial in terms of color removal. The nitrogen peroxide level was held constant at 1.5 g/bbl. The preferred order of application for maximum color removal was confirmed, namely, chlorine dioxide followed by nitrogen peroxide. Treatments with chlorine dioxide alone, and with nitrogen trichloride and benzoyl peroxide, were given for purposes of comparison and are shown in Table VII. Chlorine dioxide alone at the

rate of 1.1 g/bbl achieved a 50% color removal. Bleaching with 1.1 g chlorine dioxide followed by 1.5 g nitrogen peroxide resulted in better color removal than 2 g nitrogen trichloride and 0.048 oz benzoyl peroxide, and the latter was equaled by the above combination applied in the reverse order. The difference in color removal obtained by the preferred order of application compared with the reverse can be stated to be the equivalent of at least 0.016 g benzoyl peroxide per bbl of flour.

TABLE VII

EFFECT OF ORDER OF APPLICATION ON THE COLOR REMOVAL OBTAINED WITH CHLORINE DIOXIDE AND NITROGEN PEROXIDE IN MULTIPLE BLEACHING

Bleaching treatment per bbl of flour. Batch scale.	"Carotene"
	ppm
Unbleached patent flour	2.47
1.1 g ClO_2	1.20
1.4 g ClO_2	1.12
2 g NCl_3 plus 0.048 oz benzoyl peroxide	0.98
0.8 g ClO_2 followed by 1.5 g NO_2	1.15
1.5 g NO_2 followed by 0.8 g ClO_2	1.19
1.1 g ClO_2 followed by 1.5 g NO_2	0.86
1.5 g NO_2 followed by 1.1 g ClO_2	0.96
1.4 g ClO_2 followed by 1.5 g NO_2	0.80
1.5 g NO_2 followed by 1.4 g ClO_2	0.93

Multiple Bleaching with Chlorine and Nitrogen Peroxide. Chlorine and nitrogen peroxide treatments were studied. Typical data are presented in Table VIII. A wide range of chlorine bleaching treatments was applied with nitrogen peroxide in batch scale equipment. Very small quantities of chlorine were applied in some tests, not so much with the thought that much color removal would be achieved by the chlorine, but rather to learn whether chlorine as a precursor to nitrogen peroxide would improve bleaching efficiency. The small quantities used were not helpful, as the data in Table VIII will show.

When chlorine was used at the rate of 14, 21, and 28 g/bbl of flour with 1.5 g nitrogen peroxide, the preferred sequence of application for maximum color removal was found to be chlorine first followed by nitrogen peroxide. As was shown previously with other gaseous reagents, the difference in color removal was considerable. Thus, referring to Table VIII, when 21 g chlorine and 1.5 g nitrogen peroxide were applied to patent flour No. 1, the "carotene" value obtained by the preferred sequence was 0.85 ppm and by the reverse order 1.17 ppm. In one case flour had a commercially acceptable "carotene" level; in the other, it did not.

TABLE VIII

MULTIPLE BLEACHING WITH CHLORINE AND NITROGEN PEROXIDE IN BATCH SCALE EQUIPMENT. EFFECT OF ORDER OF APPLICATION ON COLOR REMOVAL

Bleaching treatment per bbl of flour	"Carotene"
	ppm
Patent flour No. 1	
Unbleached	2.47
0.9 g Cl_2 followed by 1.5 g NO_2	1.30
1.5 g NO_2 followed by 0.9 g Cl_2	1.30
2.7 g Cl_2 followed by 1.5 g NO_2	1.30
1.5 g NO_2 followed by 2.7 g Cl_2	1.27
14 g Cl_2 followed by 1.5 g NO_2	1.07
1.5 g NO_2 followed by 14 g Cl_2	1.16
21 g Cl_2 followed by 1.5 g NO_2	0.85
1.5 g NO_2 followed by 21 g Cl_2	1.17
28 g Cl_2 followed by 1.5 g NO_2	0.78
1.5 g NO_2 followed by 28 g Cl_2	1.03
Patent flour No. 2	
Unbleached	2.20
21 g Cl_2 alone	1.32
1.5 g NO_2 alone	1.24
2 g NCl_3 plus 0.048 oz benzoyl peroxide	0.66
21 g Cl_2 followed by 1.5 g NO_2	0.86
1.5 g NO_2 followed by 21 g Cl_2	0.96
21 g Cl_2 and 1.5 g NO_2 applied simultaneously	0.92

Summary

It has been shown that the simultaneous application of gaseous flour bleaching agents compared with a preferred order of sequential application achieved less color removal, owing to the probable interference or interaction of the two gases. This was true of nitrogen peroxide in combination with nitrogen trichloride, hypochlorous acid, chlorine, or chlorine dioxide. It was further demonstrated that in the sequential treatment of flour with the gases mentioned, a preferred order of application for maximum color removal existed for each combination of reagents. The preferred orders found were as follows:

Nitrogen trichloride followed by nitrogen peroxide.
Hypochlorous acid followed by nitrogen peroxide.
Chlorine dioxide followed by nitrogen peroxide.
Chlorine followed by nitrogen peroxide.

It may, therefore, be concluded that the greatest bleaching efficiency in multiple bleaching treatments involving nitrogen peroxide

and another bleaching gas of the group tried to date is achieved by applying the nitrogen peroxide following the other gas, say in the second of two flour agitators in series.

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MULTIPLE BLEACHING OF FLOUR. III. BLEACHING EFFICIENCY IN SYSTEMS INVOLVING NITROGEN TRICHLORIDE AND ANOTHER BLEACHING GAS[1]

C. G. FERRARI,[2] W. S. HUTCHINSON, and R. I. DERBY

General Mills, Inc., Minneapolis, Minnesota

(Presented at the Annual Meeting, May 1944; received for publication July 17, 1944)

Nitrogen trichloride is one of the most widely used commercial bleaching agents. Hence, it was thought desirable to investigate its action in the multiple bleaching of flour in conjunction with other gaseous reagents. The present paper presents further studies on multiple bleaching and will be directed specifically to nitrogen trichloride in combination with other gaseous bleaching agents except nitrogen peroxide which has been discussed in paper II of this series. In the first paper of the series by Ferrari, Hutchinson, and Mecham (1944), the multiple bleaching of flour was introduced by discussing the bleaching efficiency of the different types of bleaching equipment, including batch, pilot, and commercial scale bleaching systems. It was found that batch scale bleaching was much more efficient than the commercial mill operation. It was further shown that maximum color removal was obtained by applying gas in two or more increments rather than as a single treatment, thus permitting greater color removal with less reagent.

The second paper in the series by Hutchinson, Ferrari, and Derby (1944) discussed the bleaching efficiency of nitrogen peroxide used in

[1] Paper No. 56, Journal Series, General Mills, Inc., Research Laboratories.
[2] Present address: Standard Brands, Inc., New York.

conjunction with other gaseous bleaching agents. It was found that when nitrogen peroxide and another gas were applied simultaneously, less flour color was removed than by a sequence in which nitrogen peroxide followed the application of any one of the following reagents: chlorine, nitrogen trichloride, chlorine dioxide, or hypochlorous acid.

Apparatus and Procedures

The equipment and procedures used in these studies are discussed in papers I and II of this series. It will suffice here to say that flour color is expressed as "carotene," determined by extracting flour with water-saturated butanol and reading the color intensity of the extract in an Evelyn photoelectric colorimeter equipped with a 440-mμ filter as described by Binnington, Hutchinson, and Ferrari (1941). The "carotene" results obtained were converted to the more customary naphtha-alcohol "carotene" equivalents by means of the following equation established by Binnington *et al* in an unpublished report of the Winnipeg Grain Research Laboratory.

$$\text{Naphtha-alcohol "carotene"} = (\text{butyl alcohol "carotene"} - 0.14)\ (0.8075)$$

Experimental

Multiple Bleaching with Chlorine Dioxide and Nitrogen Trichloride. When chlorine dioxide was used in conjunction with nitrogen trichloride, different "carotene" values were obtained, depending on how the reagents were applied to flour. Simultaneous application of 0.8 g chlorine dioxide and 2 g nitrogen trichloride resulted in a "carotene" value of 0.78 ppm, as shown in Table I. Sequential

TABLE I

CHLORINE DIOXIDE AND NITROGEN TRICHLORIDE APPLIED SIMULTANEOUSLY OR SEQUENTIALLY IN THE MULTIPLE BLEACHING OF FLOUR IN BATCH SCALE EQUIPMENT

Bleaching treatment per bbl of flour	"Carotene"	Color removal
	ppm	%
Unbleached patent flour	2.20	—
2 g NCl_3 plus 0.048 oz benzoyl peroxide	0.66	70
Simultaneous: 0.8 g ClO_2 and 2 g NCl_3	0.78	65
Sequential: 2 g NCl_3 followed by 0.8 g ClO_2	0.78	65
Sequential: 0.8 g ClO_2 followed by 2 g NCl_3	0.65	70

application of nitrogen trichloride followed by chlorine dioxide gave the same "carotene" value, *i.e.*, no superiority was found. However, when 0.8 g chlorine dioxide was followed by 2 g nitrogen tri-

chloride, the "carotene" value was 0.65 ppm. For purposes of comparison, 2 g nitrogen trichloride and 0.048 oz benzoyl peroxide reduced the "carotene" value to 0.66 ppm. Thus, the preferred sequence equalled the nitrogen trichloride–benzoyl peroxide treatment in color removal.

More extended data on the effect of order of application on the bleaching efficiency of chlorine dioxide and nitrogen trichloride are given in Table II, where two patent flours and a first clear flour were

TABLE II

CHLORINE DIOXIDE AND NITROGEN TRICHLORIDE IN THE MULTIPLE BLEACHING OF FLOUR IN BATCH SCALE EQUIPMENT. EFFECT OF ORDER OF APPLICATION ON COLOR REMOVAL

Bleaching treatment per bbl of flour	"Carotene"	Crumb color score	Pekar or "slick" score
	ppm		
Patent flour No. 1			
Unbleached	2.48		Creamy yellow
2 g NCl_3 plus 0.048 oz benzoyl peroxide	0.77		10 (standard)
1.0 g NCl_3 followed by 0.8 g ClO_2	1.21		8 creamy
0.8 g ClO_2 followed by 1.0 g NCl_3	0.94		10 white
2.0 g NCl_3 followed by 0.8 g ClO_2	0.80		10 bright
0.8 g ClO_2 followed by 2.0 g NCl_3	0.78		10 bright white
Patent flour No. 2			
Unbleached	2.41		Creamy yellow
1.1 g ClO_2	1.21		11
2 g NCl_3	1.07		
3 g NCl_3 plus 0.032 oz benzoyl peroxide	0.56	10 white	12 white
2 g NCl_3 followed by 1.1 g ClO_2	0.68	10	12 white
1.1 g ClO_2 followed by 2 g NCl_3	0.49	11 white	13 bright white
First clear flour			
Unbleached	2.94		Creamy yellow
5 g NCl_3	1.20		10 (standard)
3 g NCl_3	1.98		7 creamy
1.4 g ClO_2	2.08		7 creamy
3 g NCl_3 followed by 1.4 g ClO_2	1.40		11 white
1.4 g ClO_2 followed by 3 g NCl_3	1.28		11 bright white

used in the study. Patent flour No. 1 was treated with (*a*) 1.0 g nitrogen trichloride and 0.8 g chlorine dioxide; (*b*) 2 g nitrogen trichloride and 0.8 g chlorine dioxide; using in both instances two orders of application. Bleaching with 2 g nitrogen trichloride plus 0.048 g benzoyl peroxide served as a standard. With the lower dosage of nitrogen trichloride (1.0 g) the preferred sequence for maximum color removal was chlorine dioxide followed by nitrogen trichloride. This order of application gave a "carotene" value of 0.94 ppm while the reverse order gave 1.21 ppm. When the dosage of nitrogen trichloride

was stepped up to 2 g/bbl of flour, the two sequences gave closely agreeing "carotene" values. These data illustrate an important point, namely, that the benefits of a preferred sequence of application partly disappear when the dosages of the two reagents are too greatly unbalanced, from the color removal standpoint. Thus, the ratios of the two reagents are of importance; and best results from sequential treatment are secured when the respective dosages are roughly similar in their individual effect on color removal. This fact is illustrated again by flour No. 2 in Table II. Better results from sequential treatment with chlorine dioxide and nitrogen trichloride are obtained here because the 1.1 g chlorine dioxide corresponds better to the 2 g nitrogen trichloride treatment than did the 0.8 g chlorine dioxide used with flour No. 1. The application of 1.1 g chlorine dioxide followed by 2 g nitrogen trichloride resulted in a "carotene" value of 0.49.

A first clear flour bleached with 1.4 g chlorine dioxide followed by 3 g nitrogen trichloride had a "carotene" value of 1.28 ppm, whereas the reversed sequence gave 1.40 ppm. This roughly approximates the treatment with 5 g nitrogen trichloride.

The prime consideration in flour bleaching is the baking quality of the resulting flour. It is true that adequate color removal is necessary and highly important; but, nevertheless, it is secondary to the baking characteristics of the bleached flour. It should be obvious that multiple bleaching is a flexible tool, and various combinations of reagents and treatments can be designed to give a desired result.

Sometimes certain types of flours will not tolerate much nitrogen trichloride because of adverse effects on the baking characteristics. In this case an extra quantity of costly benzoyl peroxide is customarily used to secure adequate color removal. Nitrogen peroxide, when it can be included in multiple bleaching treatments, has the virtue of cheapness, and has the added characteristic of having no measurable effect on the baking properties of the flour. The latter characteristic in some instances is very desirable. For instance, in the example cited above, a multiple bleaching treatment involving a small amount of nitrogen trichloride followed by nitrogen peroxide could be used to secure a substantial color removal and in this way keep the usage of benzoyl peroxide to a minimum, thus reducing the total cost of the bleaching treatment.

In general, the baking results secured by the use of the preferred order of application of two gaseous reagents have been at least as good as those in which the flours were bleached in the reversed order with the same reagents. Occasionally, it happens that the reversed order of application results in a flour with superior baking properties. However, the sequential application of the gaseous re-

agents in either order has resulted, in general, in flours with baking characteristics superior to those achieved by the simultaneous application of the same gases. In rare or exceptional cases it may be desirable or feasible to forego the greater color removal obtained by the preferred order of application for the better baking properties of the reversed order. It must be emphasized that such instances are few. Accordingly, the practical method is to use the preferred order from the standpoint of color removal except in the unusual cases.

Multiple Bleaching with Hypochlorous Acid and Nitrogen Trichloride. The treatment of flour with hypochlorous acid and nitrogen

TABLE III

NITROGEN TRICHLORIDE AND HYPOCHLOROUS ACID IN THE MULTIPLE BLEACHING OF FLOUR IN BATCH SCALE EQUIPMENT. EFFECT OF ORDER OF APPLICATION

Bleaching treatment per bbl of flour	"Carotene"	Color removal	pH
	ppm	%	
Patent flour No. 1			
Unbleached	2.48	—	5.80
2 g NCl_3 plus 0.048 oz benzoyl peroxide	0.67	73	5.78
2 g NCl_3 followed by 25 g HOCl	0.72	71	5.64
25 g HOCl followed by 2 g NCl_3	0.61	75	5.63
Patent flour No. 2			
Unbleached	2.41	—	5.86
2 g NCl_3 plus 0.048 oz benzoyl peroxide	0.70	71	5.84
2 g NCl_3 followed by 20 g HOCl	0.86	64	5.78
20 g HOCl followed by 2 g NCl_3	1.11	54	5.76
First clear flour			
Unbleached	2.91	—	
5 g NCl_3	1.20	59	
4 g NCl_3 followed by 15 g HOCl	1.36	53	
15 g HOCl followed by 4 g NCl_3	1.44	50	
4 g NCl_3 followed by 25 g HOCl	1.01	65	
25 g HOCl followed by 4 g HCl_3	1.21	58	

trichloride was likewise tried in various sequences. Representative data are given in Table III. With patent flour No. 1, treated with 25 g hypochlorous acid and 2 g nitrogen trichloride, the preferred sequence was in the order given. With patent flour No. 2 treated with 20 g hypochlorous acid and 2 g nitrogen trichloride, the preferred order was reversed. A first clear flour was given treatments with 4 g nitrogen trichloride and two levels of hypochlorous acid, namely, 15 and 25 g/bbl of flour. In this instance, the preferred order for maximum color removal was nitrogen trichloride followed by hypochlorous acid.

The use of hypochlorous acid at levels of 20 and 25 g/bbl of patent

flour in conjunction with nitrogen trichloride caused a lowering in pH of the order of 0.10–0.16. No effect on pH was noted owing to the order of application of the two bleaching gases.

After studying a considerable number of experimental results, some of which showed a preference for one sequence, some another, the authors have concluded that with nitrogen trichloride and hypochlorous acid, no sequence had a preponderant advantage over another from the standpoint of color removal.

Multiple Bleaching with Chlorine and Nitrogen Trichloride. Data on the simultaneous and sequential application of chlorine and nitrogen trichloride are shown in Table IV. An unbleached patent flour with

TABLE IV

CHLORINE AND NITROGEN TRICHLORIDE APPLIED SIMULTANEOUSLY OR SEQUENTIALLY IN THE MULTIPLE BLEACHING OF PATENT FLOUR IN BATCH SCALE EQUIPMENT

Bleaching treatment per bbl of flour	"Carotene"	Crumb color score	pH
	ppm		
Unbleached patent flour	2.20		6.01
2 g NCl_3 plus 0.048 oz benzoyl peroxide	0.66	10	6.03
Simultaneous: 2 g NCl_3 plus 21 g Cl_2	0.89	9C	5.84
Sequential: 2 g NCl_3 followed by 21 g Cl_2	0.91	10C	5.88
Sequential: 21 g Cl_2 followed by 2 g NCl_3	0.75	10	5.81
Sequential: 2.5 g NCl_3 followed by 21 g Cl_2	0.82		5.84
Sequential: 21 g Cl_2 followed by 2.5 g NCl_3	0.65		5.86
Sequential: 3 g NCl_3 followed by 14 g Cl_2	0.71		5.91
Sequential: 14 g Cl_2 followed by 3 g NCl_3	0.65		5.91
Sequential: 3 g NCl_3 followed by 21 g Cl_2	0.68		5.83
Sequential: 21 g Cl_2 followed by 3 g NCl_3	0.55		5.84

2.20 ppm of "carotene" was used in the experiments cited. Treatment with 2 g nitrogen trichloride and 0.048 oz benzoyl peroxide resulted in a "carotene" value of 0.66 ppm. The simultaneous application of 2 g nitrogen trichloride and 21 g chlorine gave a "carotene" value of 0.89 ppm. When the chlorine was followed by nitrogen trichloride, the color removal obtained was much greater. The reversed order gave a value substantially the same as the simultaneous application of the two gases. When the nitrogen trichloride treatment was increased to 2.5 g/bbl of flour and the chlorine kept at 21 g, the sequence of chlorine followed by nitrogen trichloride again gave better color removal. In this instance the application of the preferred sequence gave a color removal equal to the 2 g nitrogen trichloride and 0.048 oz benzoyl peroxide treatment. Continuing with 3 g nitrogen

trichloride and 14 g chlorine, and 3 g nitrogen trichloride and 21 g chlorine treatments, further confirmation of the preferred sequence was found. It will be obvious from an inspection of the data that a certain "carotene" value can be obtained in a variety of ways by manipulating the dosage of the gaseous reagents and their order of application. It remains then to choose that treatment which results in the desired baking properties. Combinations of nitrogen trichloride and chlorine caused greater changes in baking properties than was true of other gaseous reagent combinations like nitrogen peroxide and hypochlorous acid. This result was reflected somewhat by the change in pH value, the chlorine lowering pH in proportion to the quantity used. Sequence of these reagents did not affect pH to any measurable extent.

Summary

A study of nitrogen trichloride as a flour bleaching agent, applied either simultaneously or sequentially with other gaseous reagents, indicated that better color removal could be achieved with certain orders of application in sequential bleaching treatments.

Chlorine dioxide and nitrogen trichloride applied simultaneously gave about the same color removal as the same amounts applied sequentially in the order nitrogen trichloride followed by chlorine dioxide. Substantially better color removal was obtained when the sequence was reversed, namely, chlorine dioxide followed by nitrogen trichloride. Furthermore, the result applied to clear as well as to patent flours. Presumably it can be expected to apply to all intermediate grades of flour.

With hypochlorous acid and nitrogen trichloride some flours gave better color removal with one sequence, some with another. There appeared to be no consistent trend in one direction.

Chlorine and nitrogen trichloride showed a preference as to sequence for best color removal. In all feasible concentrations and with all flours, the preferred sequence was chlorine followed by nitrogen trichloride.

To summarize in tabular form, the best sequence of nitrogen trichloride and other gaseous reagents for maximum color removal was as follows:

Hypochlorous acid and nitrogen trichloride—no preferential sequence.

Chlorine dioxide followed by nitrogen trichloride.

Chlorine followed by nitrogen trichloride.

Nitrogen trichloride followed by nitrogen peroxide.

Acknowledgments

The authors wish to acknowledge the assistance of Messrs. B. A. McClellan and G. Moen in the baking phases of these experiments.

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EFFECT OF FERMENTATION, REST PERIODS, AND FORMULA INGREDIENTS ON MIXOGRAM PATTERNS [1]

JOHN A. JOHNSON and C. O. SWANSON

Kansas Agricultural Experiment Station, Manhattan, Kansas

(Received for publication June 12, 1944)

Mixograms are usually made by the continuous mixing of flour-water doughs. While this procedure gives valuable results, it does not provide direct information about the physical properties of fermented doughs nor on the influence of the usual dough ingredients on the mixogram patterns.

Johnson, Swanson, and Bayfield (1943) concluded that the greatest usefulness of the mixograms appeared to be that of furnishing information that supplements baking data. The mixograms give information regarding mixing requirements, mixing tolerance, and varietal pattern, which can be used to establish qualitative differences between flours that may or may not have different baking quality. Their conclusions were based on mixograms made on flour-water doughs.

Harris, Sibbitt, and Elledge (1944) concluded that the value of the mixograph is as an accessory tool in the evaluation of the quality of hard red spring wheat varieties. Their view was that fermentation did not change the relations between corresponding mixogram properties.

A satisfactory procedure for obtaining mixograms from soft wheat flours was described by Morris, Bode, and Heizer (1944). They used flour-water doughs with a constant absorption. They found that the areas under the mixograms consistently ranked with the generally

[1] Contribution No. 11, Department of Milling Industry.

known strength of the varieties. These mixogram areas were also highly correlated with data from other quality tests.

Harris, Sibbitt, and Banasik (1943) presented diagrams and formulas, based on mixograms from doughs fermented 3 hr, for calculating the loaf volumes. Such a high correlation was found between the calculated and the actual volumes as to render possible the prediction of loaf volume by the use of the regression equation.

The objectives of the present investigation were to obtain additional information on the changes in mixogram patterns resulting from the addition of the various ingredients used in baking and the effect of the process of yeast fermentation. Since the mixogram patterns of flour-water doughs are also influenced by the rest periods (Swanson, 1940), it was necessary to compare those made from fermented and unfermented doughs after rest periods equal to the fermentation time. The effect of fermentation on mixograms from various wheat varieties was also determined. Since baking data were available for these varieties, the relationship between mixogram measurements and baking data were calculated.

Materials and Methods

A composite, 12.9% protein and 0.42% ash, consisting of several experimentally milled and thoroughly blended hard winter wheat flours representing several varieties, was used. For work on individual varieties, samples were available from the 1943 crop. Turkey, Tenmarq, Pawnee, Chiefkan, and Early Blackhull were chosen because they represented wide variations in mixogram patterns. This group of samples also represented a range in protein content. The National Mixograph was geared to a speed of 89 rpm and a No. 9 spring setting was employed except for the fermented-dough mixograms of flours from the varieties where a No. 11 setting was necessary. A total of 35 g of flour (15% moisture basis) was used for each mixogram except where part of the flour was replaced by other ingredients such as dry milk solids and shortening in order to keep total dry matter constant. The absorption of the flours was calculated on the basis of the protein content. The mixograms were made in an air-conditioned room maintained at a temperature of 80°F. After fermentation of the sponges in the mixograph bowls, the same were placed in the machine and the mixogram made. Three types of mixograms were made from doughs described as flour-water, rest, and sponge, and the mixograms will be differentiated by these terms. Those made by continuous mixing of flour-water doughs are designated as no rest dough, those made on doughs for which there was a rest period with no yeast fermentation, as rest doughs, and those made after yeast fermentation, as sponge

doughs. The only difference between the rest and the sponge doughs was the omission of fermentation in the former.

For mixograms testing the effects of fermentation or rest periods, 70% of the flour, and water representing 80% of the total absorption, and such other ingredients as were being studied or that are normally added to the sponge were placed in the mixograph bowl. The initial mixing of the sponge was for 0.5 min, which was found to be long enough to incorporate all the ingredients. The bowl containing the dough for the sponge was placed in a fermentation cabinet maintained at 30°C and at 80% relative humidity. After 3-hr fermentation or 3-hr rest, the bowl with the sponge or the rest dough was placed in position on the mixograph, the remaining flour, water, and the other formula ingredients added, and the mixogram made. The pen was prevented from the first strong upward swing by placing the thumb momentarily on the dampening device of the mixograph.

Results and Discussion

The experimental results are presented in six figures and two tables. The general arrangement of the mixograms in the figures is such as to obtain comparisons of the effects of 3-hr rest period and 3-hr fermentation in the sponge with those obtained by continuous mixing of no rest doughs. The effect of each ingredient, other than flour and water,

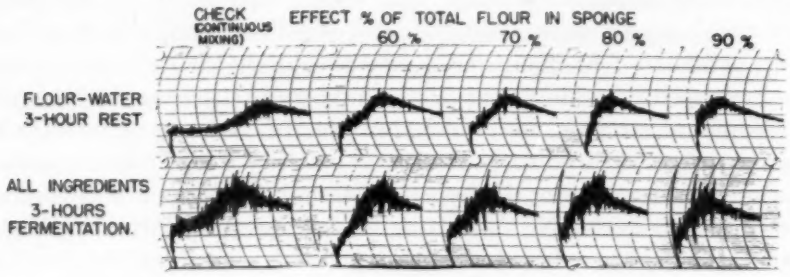


Fig. 1. Effect of 3-hr rest and 3-hr fermentation periods with various percentages of flour in the sponge.

is shown by each one being present separately in the no rest doughs, rest doughs, and sponge doughs. A separate group of mixograms (Fig. 1) shows the effect of all the ingredients in the sponge as well as the effect of the percentage of flour in the sponge.

The data for making the calculations presented in Tables I and II were taken from flour-water and sponge dough mixograms and the baking results obtained in connection with the testing of varieties.

Effect of Percentage of Total Flour during the Rest Period or during Fermentation (Fig. 1). These mixograms were made to determine the most useful percentage of the total flour which should be present

the doughs both for the rest periods and for the fermentation of the sponge. The upper line shows the effect of the presence of 60%, 70%, 80%, and 90% of the total flour during the 3-hr rest periods in comparison with the check mixogram obtained with continuous mixing of no rest flour-water dough. The appearance of the mixograms obtained indicated that 70% flour would be most useful. The times to reach the curve peak decreased more and more as the percentage of flour in the rest doughs increased. As more and more flour was wetted in the rest or sponge doughs, less was left to be wetted in the final mixing. The time required to reach the peak after the 3-hr rest period as compared with the much longer time for the one no rest dough is in line with results reported by Swanson and Andrews (1945). Further comparisons will be made later on the effects on mixogram patterns of rest periods without fermentation and effects on patterns obtained after fermentation. The effects of the rest periods will be found to be about as marked as the effect of fermentation.

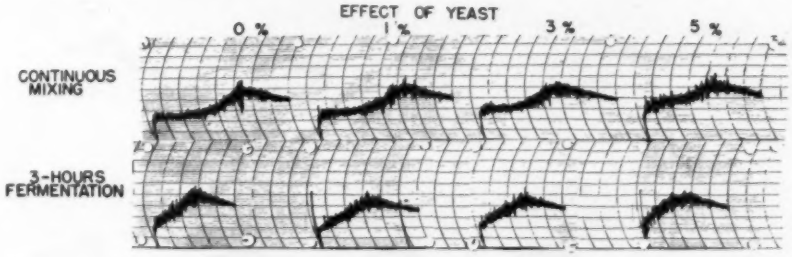


Fig. 2. Effect of continuous mixing and of 3-hr fermentation with various percentages of yeast.

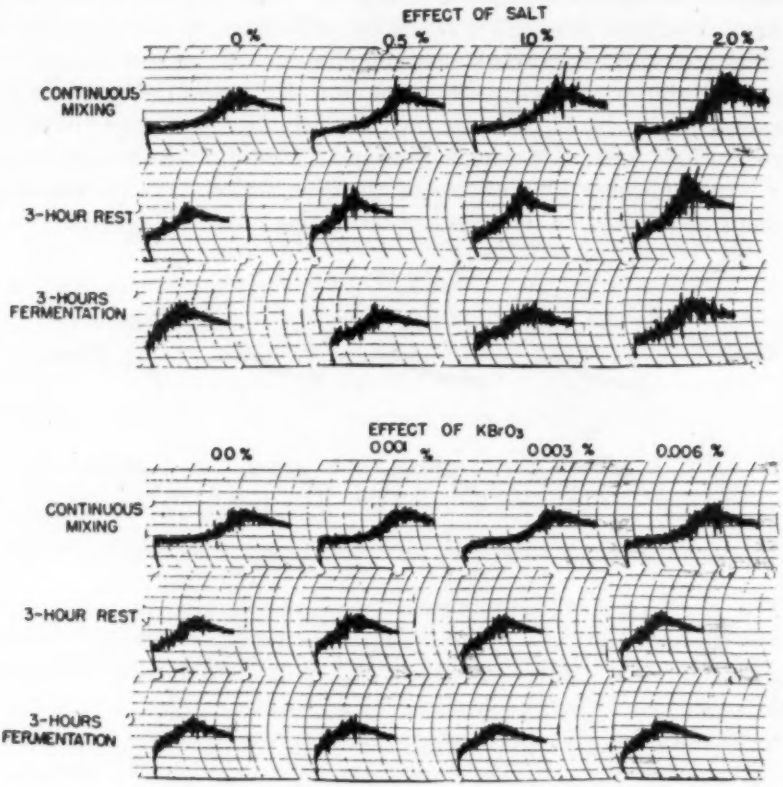
The effect of 3-hr fermentation (with the various percentages of flour in the sponges and with all the formula ingredients present: yeast, salt, $KBrO_3$, milk, shortening, sugar, and malt) was to raise the height of the peak and widen the band of the mixogram. The time to reach the peak was slightly decreased as the percentage of the flour in the sponges increased. The effect of each ingredient on the mixogram pattern will be shown in the following figures.

Effect of Percentage Yeast (*Fig. 2*). The mixograms in line 1 were made on no rest doughs and those in the second line on 70% sponge doughs after 3-hr fermentation. The yeast itself without fermentation caused very little change in the patterns except a slight decrease in the time to reach the peak when as much as 5% was present. Accordingly, without fermentation the 3% yeast normally used can be considered to have no material effect on the pattern.

After 3-hr fermentation (line 2, Fig. 2) the patterns were markedly different from those obtained with continuous mixing. But the dif-

ferences between the mixograms obtained after fermentation with 1%, 3%, and 5% yeast were only slightly different from the check mixogram (Fig. 1, line 2) obtained from a rest dough. Thus, it was not the yeast nor the process of fermentation that resulted in the changes in the patterns, but the effects incident to duration of time, or rest, between the initial and final mixing.

Effect of Sodium Chloride and of Potassium Bromate. The mixograms in Figure 3 show that increasing percentages of sodium chloride



F g. 3. Effect of salt and of $KBrO_3$ with continuous mixing, 3-hr rest, and 3-hr fermentation periods.

increase the band width and the heights. Three-hr fermentation as compared with 3-hr rest results in slightly longer times for development and lower heights. Concentrations of potassium bromate up to 0.006% did not alter the patterns for no rest, rest, or sponge doughs. In usual baking tests 0.006% of potassium bromate with no milk present would likely cause a bucky dough. Such an effect was not apparent in these patterns.

Effect of Sugar and Malt (Fig. 4). The sugar decreased somewhat

the time to reach the top of the mixograms for the no rest doughs. The mixograms made after 3 hr of rest and those made after 3-hr fermentation are almost identical in heights and in the notably shorter time to reach the peaks as compared with the continuous mixing. The stimulating effect of sugar on yeast activity during fermentation is only slightly shown in the patterns obtained. The malt (120°L) had very nearly the same effect as sugar on mixograms for no rest doughs. The 3-hr fermentation period reduced the heights somewhat

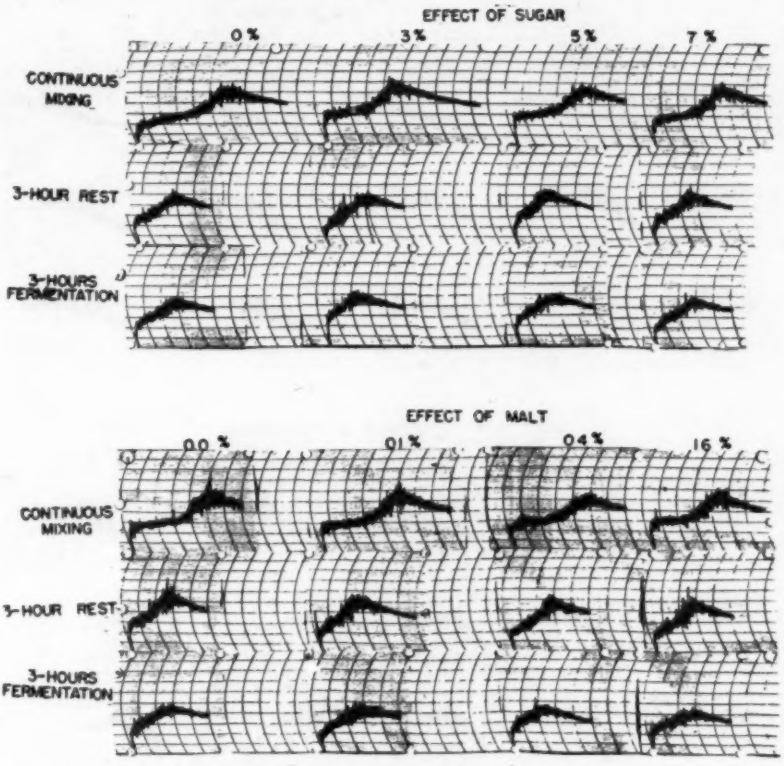


Fig. 4. Effect of sugar and malt with continuous mixing, 3-hr rest, and 3-hr fermentation periods.

more than the rest periods. Both rest and fermentation reduced the heights and the development times as compared with the no rest dough.

Effect of Milk and Shortening (*Fig. 5*). The effect of milk was mostly in the increase of band width of all the mixograms. The mixograms obtained after 3 hr of rest and after 3 hr of fermentation are notably similar, but markedly different from those obtained from the no rest doughs. Various percentages of hydrogenated shortening show no apparent effects on the mixogram patterns, since those with 4% are almost identical with those in which this ingredient was absent.

This agrees essentially with the results obtained by Shellenberger (1941).

Mixograms from the Variety-Protein Series (Fig. 6). In Figure 6 mixograms obtained from no rest flour-water doughs are compared with those obtained after 3-hr fermentation of sponge doughs containing all the formula ingredients. As the protein content of the flours increases, the heights increase and the times to reach the peaks are shortened. The degree of differentiation among the varieties, as shown by the

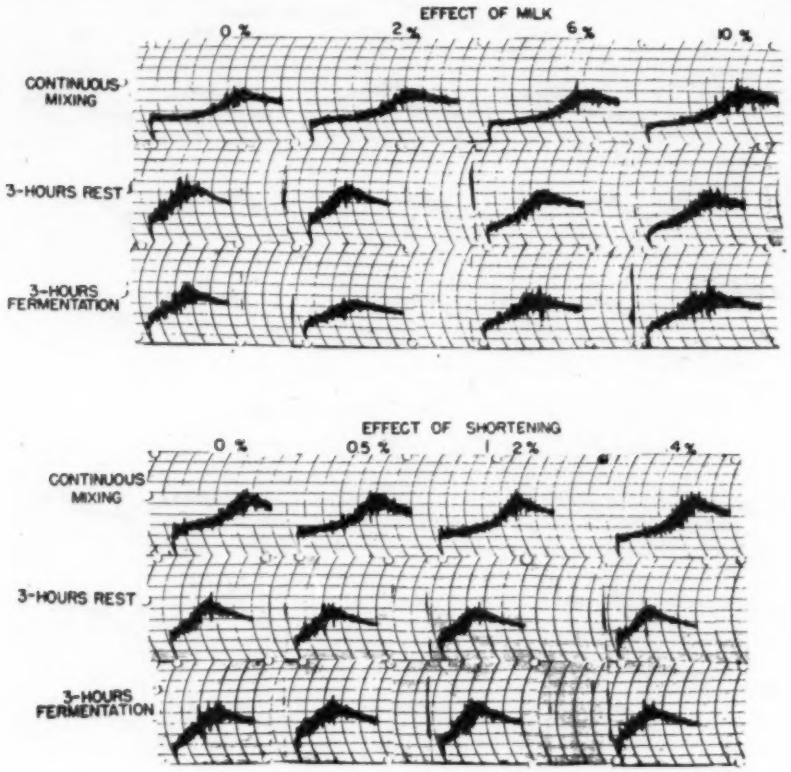


Fig. 5. Effect of milk and shortening with 3-hr rest and 3-hr fermentation periods.

mixograms of sponge doughs, is less than that shown by those from no rest doughs. That is, the formula ingredients together with the rest period incident to the fermentation process tend to decrease differences from variety.

Statistical Comparisons of Mixogram Properties from Varieties. The degree of association between the mixogram characteristics obtained from no rest doughs and those obtained from sponge doughs was tested by computing correlation coefficients between various measurements which were made on the variety mixograms. The measure-

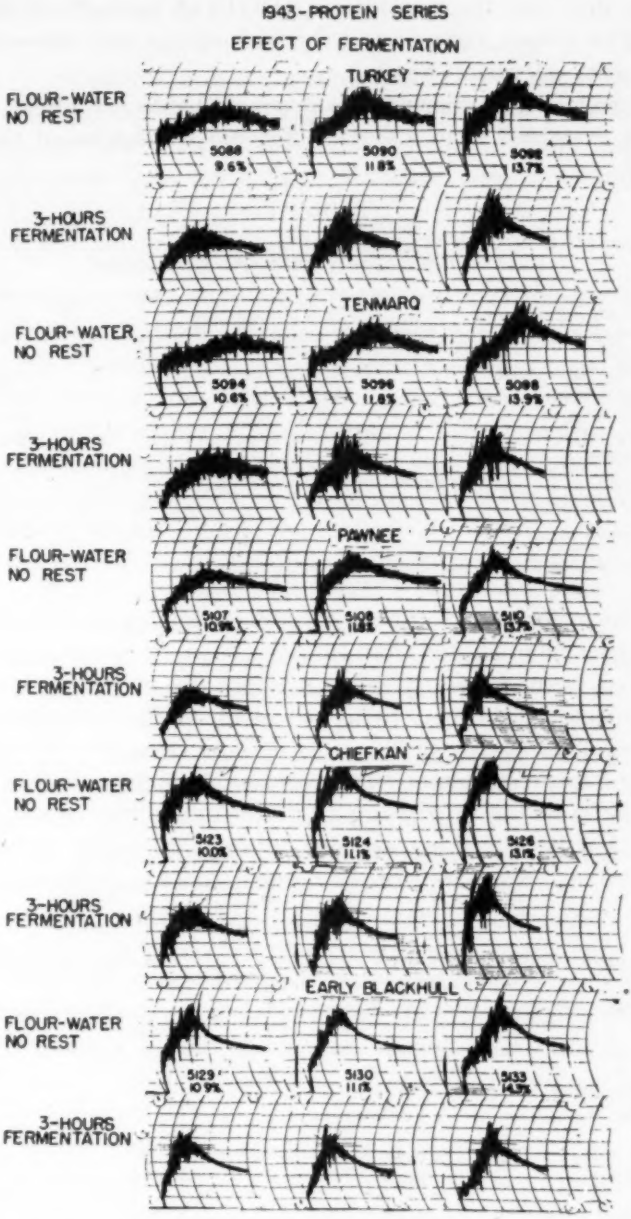


Fig. 6. Mixograms as influenced by variety, protein content, and 3-hr fermentation.

ments taken, as described by Swanson and Johnson (1943), were: mixing time in minutes, height in chart units, development angle (DOW) in degrees between the ascending slope and a horizontal line, weakening angle (WON) in degrees between the descending slope and a

horizontal line, and the supplement (DOT) of the sum of these two angles. The protein content and the loaf volume data were available from the work on variety testing.

The correlation coefficients are given in Table I. These relationships were examined from a scatter diagram and appeared essentially linear.

TABLE I

CORRELATION COEFFICIENTS BETWEEN CHARACTERISTICS OF NO REST AND FERMENTED DOUGH MIXOGRAMS

No rest	3-hr fermentation	
x	y	r_{xy}
Mixing time, min	Mixing time, min	+0.62
Height, units	Height, units	+0.64
DOW,[1] deg.	DOW, deg.	+0.71
WON,[2] deg.	WON, deg.	+0.73
DOT,[3] deg.	DOT, deg.	+0.79
N = 53	5% level of significance = 0.27	

[1] Development angle.
[2] Weakening angle.
[3] Supplement of sum of development and weakening angles.

The characteristics of the sponge dough mixograms can only to a limited degree be predicted from those made on no rest doughs. However, as has been shown, it is not the process of fermentation itself but the effects of the rest period incident to fermentation and the formula ingredients that produce the marked changes.

The correlations between loaf volume, protein content, and the characteristics of the mixograms from no rest and sponge doughs are given in Table II. The correlations between the height units and the protein content are greater for the no rest than for the sponge doughs,

TABLE II

CORRELATION COEFFICIENTS BETWEEN MIXOGRAM CHARACTERISTICS, PROTEIN CONTENT, AND LOAF VOLUME

		No rest	3-hr ferm.
x	y	r_{xy}	r_{xy}
Height, units	Protein %	+0.63	+0.49
Height, units	Loaf vol. cc	+0.13	+0.49
WON,[1] deg.	Protein %	+0.35	+0.32
WON,[1] deg.	Loaf vol. cc	+0.16	+0.02
DOT,[2] deg.	Protein %	+0.61	+0.31
DOT,[2] deg.	Loaf vol. cc	+0.19	+0.20
Loaf vol. cc	Protein %		+0.81
N = 53	5% level of significance = 0.27		

[1] Weakening angle.
[2] Supplement of sum of development and weakening angles.

but the correlations between the height units and loaf volume are greater for the sponge doughs. The correlations between loaf volume and the development and weakening angles were not significant for either the straight or the sponge doughs. No mixogram characteristic is as highly correlated with the baking value as is the protein content. This corroborates the findings of Johnson, Swanson, and Bayfield (1943).

Summary and Conclusions

The mixogram patterns obtained on no rest doughs, continuous mixing, differ markedly from those obtained after rest or fermentation periods. The patterns of the mixograms obtained on flour-water doughs after rest periods of 3 hr were nearly the same as those obtained from sponge doughs after 3 hr of fermentation. The rest period and the fermentation process each markedly shortens the time to reach the mixogram peak and increases the steepness of the ascending and of the descending slopes. Thus the rest periods produce about as great an effect on patterns as the process of yeast fermentation.

When all the ingredients were present in the sponge during the fermentation period, the height and the band width were increased—sodium chloride having the greatest effect, potassium bromate and shortening having none. The effect of yeast, sugar, and malt was small but that of milk moderate.

Mixogram patterns from sponge doughs of the various varieties differ less than those from no rest doughs, but the varietal effect can be clearly observed. While the mixing times of Tenmarq and Turkey are shortened in the fermented sponge doughs, they still remain longer than for Chiefkan and Early Blackhull.

This limited investigation indicates that if mixograms are used to obtain accessory or preliminary information on flours, the choice between no rest and sponge dough mixograms will depend upon the use of the flour. With the sponge method of baking, the mixogram made on sponges would appear to be more useful, and with the straight dough method of baking, those from no rest dough would apparently be better.

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THE EFFECT OF MIXING SPEED AND DRY MILK SOLIDS ON BREAD VOLUME [1]

EMERY C. SWANSON and E. G. BAYFIELD

Kansas State College, Manhattan, Kansas

(Read at the Annual Meeting, May 1944; received for publication November 10, 1943)

In view of the widespread use of dry milk solids in commercial bakeries, and even in laboratory test baking, it is surprising that the literature contains relatively little data on the effect of this ingredient on baking practice. The authors' interest in this matter was aroused when it was brought to their attention [2] that instances of improved results from doughs containing dry milk solids were observed when slow rather than high speeds were used for mixing. An investigation of the relations between mixing speeds, milk solids, and bread quality therefore appeared to be worth undertaking.

A brief study of the problem by H. S. Myers [3] indicated that a poorer loaf of bread resulted when the mixing speed was decreased below the level normally used in the laboratory. This and other findings, coupled with results obtained with high-speed commercial mixers, suggested the existence of optimum mixing speeds for specific classes of doughs. Further experiments then indicated that the optimum speed changed with the amount of dry milk solids used in the formula. The more comprehensive study reported in this paper was therefore begun.

The literature relating to this subject is scant. Papers reviewed here deal also with some effects of bromate, since this had to be considered in the investigation. In 1936 Bohn and Bailey found that

[1] Contribution No. 107, Department of Milling Industry. The paper is based on a thesis submitted to the graduate faculty, Kansas State College, in partial fulfillment of the requirements for the degree of Master of Science.
[2] Personal communication from Mr. Roud McCann, Director of the American Dry Milk Institute.
[3] Unpublished data, Department of Milling Industry, Kansas State College.

excessive mixing of a dough beyond optimum development produced inferior bread, and that high-speed mixers developed dough more quickly than low-speed mixers. Stamberg and Bailey (1938) found optimum mixing times for each speed of rotation of the mixing blades. They also noted that the inclusion of 6% of dry milk solids in bread dough increased the mixing time and increased the tolerance to variations in mixing speed. The optimum speed of mixing for the Hobart-McDuffee mixer was reported to be between 60 and 80 rpm. Ofelt and Larmour (1940) found that the addition of dry milk solids created a tolerance to bromate which tended to prevent damage to loaf volume and to grain and texture when relatively large dosages were used.

Larmour and MacLeod (1929) and Geddes and Larmour (1933) had shown earlier that a bromate formula gave a better measure of baking value than the basic formula. Geddes and Larmour (1933) noted that bromate response was somewhat dependent on protein content. More recently, Barmore, Finney, and McCluggage (1941, 1942) demonstrated the existence of an optimum bromate requirement for flours and showed that the optimum varied for different varieties of wheat. These various investigations indicated that the problem of determining the best mixing speeds and times for specific doughs would be complicated not only by the amount of dry milk solids included in the formula, but also by the amount of bromate.

Materials and Methods

The investigation was made with three flours milled on a commercial 65-bbl mill from Tenmarq and Chiefkan wheats, and from a sample representing a commercial mix. Analytical data on these flours and on the dry milk solids used in the investigations are given in Table I.

TABLE I

CHEMICAL ANALYSES OF FLOURS AND DRY MILK SOLIDS
(Mean data for several random samples; as received moisture basis)

Material	Protein	Moisture	Ash
	%	%	%
Tenmarq flour	12.2	11.6	0.50
Chiefkan flour	12.9	11.7	0.43
Commercial flour	12.0	11.9	0.49
Dry milk solids	30.8	3.5	7.93

Here and throughout the paper, "dry milk solids" refers to the product made by removal of the water and fat from milk; the product contains not over 1.5% fat and not over 5% moisture.

Four levels of dry milk solids—0, 2, 6, and 12%—were studied with the following commercial-type formula: 6 g sugar, 1.5 g salt, 3 g

shortening, 2 g yeast, and 0.25 g malt syrup (120° Lintner). Bromate was added in the amount required to give optimum loaf volume when the proportions of the other ingredients had been fixed, and absorptions were adjusted to give optimum dough-handling properties. The procedures used for determining bromate requirements and absorptions are discussed later.

Three mixing machines were used: (1) the Swanson-Working mixer, which has a four-arm planetary mixing head and two stationary arms, (2) the Hobart-McDuffee mixer, which has a two-arm planetary mixing head and one stationary arm, and (3) the experimental model of the Working mixer, which has a two-arm planetary head and three stationary arms. Mixing speeds of 50, 75, 100, 125, 150, 175, 200 rpm were used on the Swanson-Working and Working mixers, and 40, 70, 100, and 130 rpm on the Hobart-McDuffee. The mixing effects of the Hobart-McDuffee machine within its range of speeds are approximately the same as those of the other two mixers within their ranges. Twin-loaf doughs were mixed in the Swanson-Working and Hobart-McDuffee mixers, but single-loaf doughs were mixed in the Working mixer because of its limited capacity.

Low-form, commercial-shaped pans were used throughout the investigation. Fermentation temperature and humidity were maintained at 30°C and 75 to 80% respectively. The procedures recommended by the A.A.C.C. were followed for fermentation, punching, proofing, and baking. Loaf volumes were taken immediately after baking, and grain and texture of the bread were observed the following day to make certain that the bread was commercially acceptable.

General Plan of Investigation

Each of the three flours (Tenmarq, Chiefkan, and commercial) was used in studies with the Swanson-Working and Hobart-McDuffee mixers, but only Tenmarq flour was used with the Working mixer. Thus, there were seven flour-mixer groups.

Within each group, studies were made with four levels of dry milk solids (0, 2, 6, and 12%) and at all the previously mentioned speeds of the mixer. For the Swanson-Working mixer there were thus 84 combinations representing three flours, seven speeds, and four levels of dry milk solids; for the Hobart-McDuffee mixer there were 48 combinations representing three flours, four speeds, and four levels of milk solids; and for the Working mixer there were 28 combinations representing one flour, seven speeds, and four levels of milk solids. There was, therefore, a total of 160 combinations, and 12 replicate loaves (total 1,920) were baked for each of these.

Adjustment of Absorption and Bromation

When the investigation was outlined it was realized that the optimum absorption, bromation, and mixing times would probably vary within the set of 160 combinations outlined above. However, it was not practical to vary these three additional factors, as even with two levels of each the investigation would have been increased eight times. Accordingly, the optimum absorption, bromation, and mixing times were determined in preliminary experiments.

The absorption was varied only with the flour and the amount of dry milk solids used in the formula. Optimum absorption was determined by handling properties as judged by an experienced baker; a dough with the amount of water thus determined was then mixed in the mixograph and the height of the curve was noted; the absorptions for the milk-containing doughs were then adjusted until they gave mixograms of the same height as those of the no-milk doughs.

TABLE II

Absorptions Used with Each Flour at Each Level of Milk Solids

Milk solids	Flour		
	Tenmarq	Chiefkan	Commercial
%	%	%	%
0	62.5	67.0	62.0
2	65.0	68.5	64.0
6	66.5	71.0	65.5
12	67.5	71.0	66.5

Data on the optimum absorptions are recorded in Table II. The relation between absorption and dry milk solids is curvilinear for all three flours; that is, less water per unit of dry milk solids was added at the 12% level than at the 6% and lower levels. In this connection it should be noted that the dry milk solids used throughout the study had a lower water-absorbing ability than normal.

Bromate requirements were also determined for each flour at each level of milk solids. The optimum requirement was first estimated and loaves were baked at that level of bromate, and with 1 mg less and with 1 mg more. If the loaf representing the estimated optimum bromation was the largest, the estimate was assumed to be correct; if either of the other doughs yielded a larger loaf, a further experiment was made to determine the optimum (see Table III).

Effect on Mixing Times

Optimum mixing times were determined for each of the 160 combinations by much the same method as that used for estimating broma-

TABLE III

DATA ON BROMATION

Milk solids	Potassium bromate per 100 g flour		
	Tenmarq	Chiefkan	Commercial
%	*mg*	*mg*	*mg*
0	1	4	2
2	3	6	4
6	4	7	5
12	4	7	5

tion. A dough for a given combination was observed during mixing, and this was stopped as soon as the dough appeared to be fully developed, that is, as soon as it had a smooth texture and dull surface, and felt dry when handled. Immediately thereafter two corresponding doughs were mixed for three fourths and five fourths of the estimated optimum mixing time. All three doughs were baked. If the loaf representing the estimated optimum was the largest, the estimate was assumed to be correct; if not, a further experiment was made.

Data showing the relations between mixing times and percentage of dry milk solids are graphed in Figure 1. The three graphs at the top represent Tenmarq, commercial, and Chiefkan flour, mixed in the Swanson-Working machine; corresponding graphs for the Hobart-McDuffee machine are in the bottom row. The Working mixer, which was used only with Tenmarq flour, gave results that differ little from those obtained with the Swanson-Working mixer, and these data need not be recorded.

At all speeds of the mixers, the relation between mixing time and dry milk solids is linear within the limits of experimental error. With the slower speeds, optimum mixing time increases with increasing amounts of dry milk solids. As speed is increased there is a lessened effect of dry milk solids on mixing time, and at highest speeds the increase is barely perceptible.

There are interesting differences between the three flours. It is best to examine first the graphs for the Swanson-Working mixer, and at the initial points (No. D.M.S.) on the group of curves for each flour. It will be noted that mixing speeds have much less effect upon the time needed for optimum development with Chiefkan than with the other two flours, with Tenmarq showing the greatest range. Essentially the same results are shown by the data for the Hobart-McDuffee mixer. In effect it thus appears that Tenmarq dough develops comparatively slowly at low mixing speeds as compared with Chiefkan. However, so far as these two flours are concerned, Chiefkan obviously requires less mixing at any speed than does Tenmarq. Between Tenmarq and the

commercial flour, differences are less apparent at high speeds, but at low speeds Tenmarq requires longer mixing.

The mixing requirements of all three flours are affected in much the same way by the addition of dry milk solids. This ingredient increases the spread in the time needed when using different mixing speeds. With the Hobart-McDuffee mixer, the spread for 12% milk solids for each flour is roughly proportional to the corresponding spread when using no milk solids. The same generalization holds with respect to Tenmarq and Chiefkan with the Swanson-Working mixer. However,

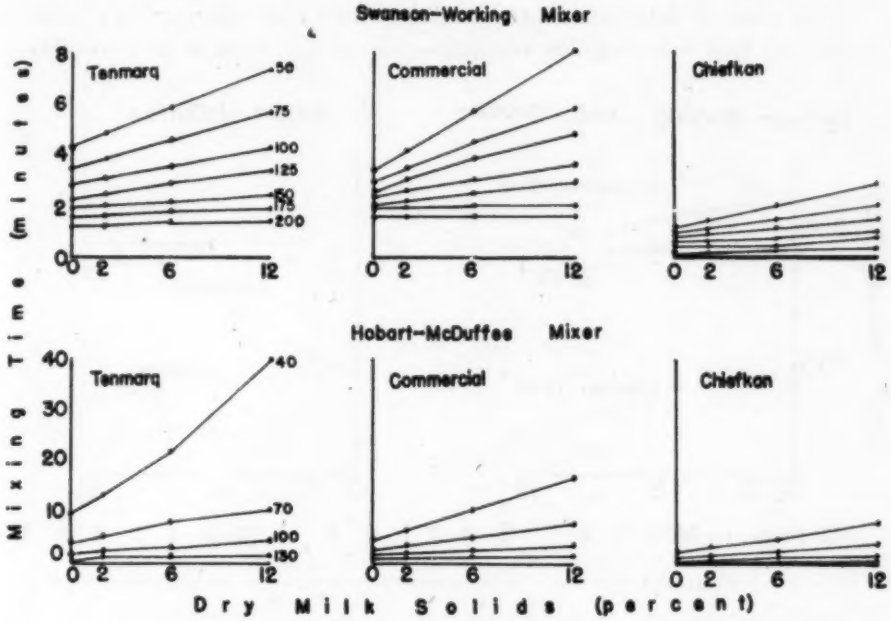

Fig. 1. Graphs illustrating the relations between optimum mixing time and percentage of dry milk solids at different mixing speeds.

with this mixer, the commercial flour appears to react somewhat differently. At high speeds its behavior when milk solids are added is similar to that of Tenmarq. But at low speeds, the commercial flour shows a proportionately larger increase in mixing time with added milk solids. This anomaly is difficult to interpret. If the Swanson-Working data alone are considered, it appears that the addition of milk solids makes the mixing requirements of the commercial flour much more similar to those of Tenmarq flour than they were with no milk solids. But the Hobart-McDuffee data do not confirm this hypothesis. These results seem to indicate that flours to which variable amounts of milk solids are added react differently to the two types of mixers. The

loaf volume data do not support the conclusion of Stamberg and Bailey (1938) that the addition of milk solids increases the tolerance to mixing speed.

Effect on Loaf Volumes

Data showing the effect of dry milk solids on loaf volumes are summarized in Figure 2. Curves for the Swanson-Working mixer, and the single curve for Tenmarq and the Working mixer, are shown on the left. The Hobart-McDuffee curves are shown on the right. Each curve represents the mean data over all mixing speeds.

No general statement can be made about the effect of dry milk solids on loaf volumes, for the varieties do not behave in a similar

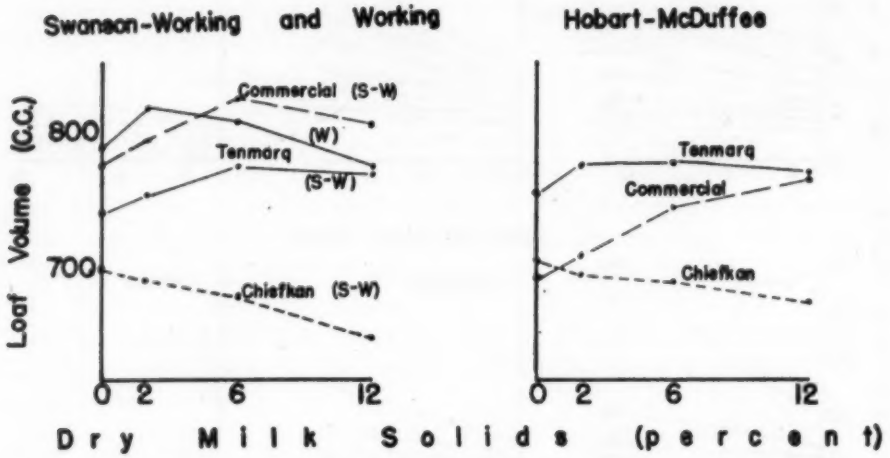

Fig. 2. Graphs illustrating the average relation between loaf volume and percentage of dry milk solids.

manner. With Chiefkan, the addition of increasing amounts of milk solids causes a steady decrease in loaf volume; this is shown by data for both mixers. With the commercial flour and the McDuffee mixer, the curve rises steadily; but with the Swanson-Working a maximum loaf volume is shown at 6% of dry milk solids. Moreover, with the Swanson-Working mixer the commercial flour gives higher loaf volumes at all levels of milk solids than it does when mixed in the Hobart-McDuffee machine.

The differences between the curves for Tenmarq mixed in the three machines are not very large. There are some differences both in the general level and the shapes of the curve, but each indicates a slight maximum at either 2% or 6% of milk solids.

In view of the distinctive behavior of Chiefkan it seems safe to conclude that some varieties will show characteristic differences in the

response of loaf volumes to added dry milk solids. Moreover, it is also clear that mixing conditions have a decided effect on the response of loaf volume to added milk solids.

The last statement can be supported with the aid of the more detailed data for the Swanson-Working and Hobart-McDuffee mixers given in Figure 3. For the former, curves for five rather than seven speeds are shown to simplify the graphs. The Chiefkan data can be dismissed briefly; they show that mixing speed and type of machine

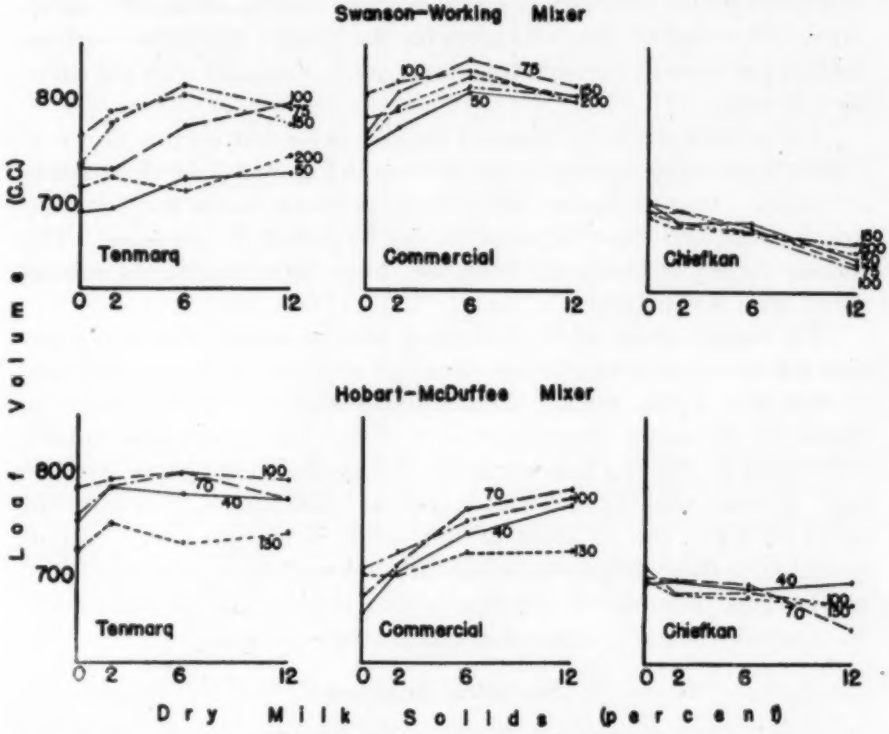

Fig. 3. Graphs illustrating the relations between loaf volume and percentage of dry milk solids at different mixing speeds.

had comparatively little effect on the relation between loaf volume and dry milk solids.

The maximum effect of mixing speed on the relation is shown by the Tenmarq graph in the top left corner. If minor irregularities are disregarded, it appears that loaf volume increases with an increase of mixing speed from 50 rpm through 75 to 100 or 125 rpm; but the curve for 200 rpm falls back almost to the level of 50 rpm. Moreover, whereas the curves for 50 and 75 rpm rise steadily with increasing milk solids, the curves for 100 and 125 rpm show maxima. In some respects the

Tenmarq curves for the Hobart-McDuffee mixer show a similar pattern; loaf volumes increase from 40 through 70 to 100 rpm, and decrease sharply at 130 rpm. However, no consistent changes in the shapes of the curves are apparent.

Data for the commercial flour are intermediate between those for Tenmarq and Chiefkan; they are more regular than the former and less regular than the latter. With both machines, one of the intermediate speeds give higher loaf volumes than either the slowest or fastest speeds. All curves for the Swanson-Working machine show a maximum—sometimes rather slight. But all curves for the Hobart-McDuffee machine tend to rise steadily, though this rise is much less rapid with the curve for 130 rpm.

The general similarity between the curves for loaf volume shown in Figure 3 and those for mixing times shown in Figure 1 is worth a passing comment. In both figures the spreads between curves for Tenmarq are greatest and those between curves for Chiefkan are least. The former variety is obviously influenced more by changing the mixing speed than is the latter.

The results of the study as a whole suggest that further investigation will be required to establish the exact relations between percentage of dry milk solids, mixing times, mixing speeds, and loaf volumes. There are obviously clear-cut varietal differences in response to milk solids, and studies of a larger number of varieties should prove interesting. Mixing conditions are also important, and changes in these do not affect all flours and all levels of milk solids in the same way. In all probability, these differential effects are governed by regular principles, but it seems premature to attempt to state these even as hypotheses on the basis of the data collected in this preliminary study.

Statistical Analyses

It was found that the variation in loaf volumes within each flour-mixer group was related to the mean loaf volume for the group. Accordingly, it was necessary to analyze the variance for each group separately. The resulting statistics are given in Table IV.

Significant effects of level of milk solids and of mixing speed occurred with each flour and each mixer. With both commercial and Chiefkan the effects of milk solids were far greater than those of mixing speeds (*cf.* Figure 3). But with Tenmarq, mixing speeds had the greater effect, except with the Working mixer, in which the effects of milk solids and speeds were about equal.

In five of the seven groups, significant interactions between milk solids and mixing speeds occurred. Significant interactions might well

TABLE IV

ANALYSES OF VARIANCE OF DATA ON LOAF VOLUME FOR VARIOUS MIXING SPEEDS AND LEVELS OF DRY MILK SOLIDS

Varieties	Source of variation	Mixer					
		Swanson-Working		Hobart-McDuffee		Working	
		Degrees of freedom	Mean square	Degrees of freedom	Mean square	Degrees of freedom	Mean square
Tenmarq	Milk solids	3	16,443**	3	5,439*	3	32,382**
	Speeds	6	57,939**	3	25,851**	6	31,620**
	MS × S	18	5,222**	9	1,215**	18	2,914**
	Replicates	308	218	177	278	308	278
Commercial	Milk solids	3	31,480**	3	52,807**		
	Speeds	6	4,187**	3	7,207**		
	MS × S	18	1,629**	9	1,247**		
	Replicates	308	235	177	127		
Chiefkan	Milk solids	3	32,938**	3	13,812**		
	Speeds	6	291*	3	493**		
	MS × S	18	489**	9	1,942**		
	Replicates	308	61	177	51		

* Denotes the 5% level of significance is exceeded.
** Denotes the 1% level of significance is exceeded.

have been demonstrated in the other two groups had the replicate errors been lower. Accordingly, it appears that the effect of mixing speed on loaf volume may vary somewhat with the level of milk solids in the dough. The statistics thus serve to confirm the conclusions based on inspection of the figures presented in the foregoing section.

Summary

Flours milled from Tenmarq, Chiefkan, and a commercial wheat mix were studied with four levels of dry milk solids (0, 2, 6, and 12%) and with seven mixing speeds in the Swanson-Working mixer, and with four speeds in the Hobart-McDuffee mixer. The Tenmarq sample was also studied at seven mixing speeds in the Working mixer. Data were collected on optimum mixing times and on loaf volumes.

At all speeds of all machines, optimum mixing time increased with increasing milk solids, but the increase was very small at high speeds. In general, at all speeds and levels of milk solids, Tenmarq required longer mixing times than Chiefkan, and the commercial flour held an intermediate position.

Loaf volumes for Chiefkan were consistently reduced by added milk solids, but those for the other two flours were improved. In all three mixers Tenmarq yielded maximum loaf volumes at intermediate levels

of milk solids. Flour from the commercial mix showed a maximum loaf volume at 6% milk solids in the Swanson-Working machine, but loaf volume increased steadily with increased milk solids when mixed in the Hobart-McDuffee machine. The detailed data emphasize the characteristic differences between the flours. They also show that mixing conditions have an important effect.

Further investigation will be required to elucidate the principles that govern the complex relations between mixing times, mixing speeds, dry milk solids, and loaf volumes.

Acknowledgments

Thanks are due to the American Dry Milk Institute, Chicago, Illinois, for supporting the research assistantship under which part of this work was done, to Dr. E. B. Working for consultation during the experimental work, and to Dr. H. C. Fryer for his assistance with the statistical treatment of the data.

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VARIETAL RESPONSES TO CERTAIN BAKING INGREDIENTS ESSENTIAL IN EVALUATING THE PROTEIN QUALITY OF HARD WINTER WHEATS [1]

K. F. FINNEY and M. A. BARMORE [2]

(Presented at the Annual Meetings, May 1939 and May 1941; received for publication June 28, 1944)

The adequacy of most baking methods used for evaluating the protein quality of hard winter wheat flours, especially those experimentally milled from different varieties, has long been questioned. These baking methods, for the most part, have not been formulated on the basis of flour requirements and flour responses to certain important ingredients and treatments. For example, it seems to have been fairly well demonstrated that hard winter wheat flours require bromate, but there is a decided lack of information as to the requirement of individual varieties. Similarly, the need for malt syrup or malted wheat flour has been demonstrated, but the response to this ingredient, to milk solids, and to potassium bromate, singly and in various combinations with the other generally accepted basic ingredients, has not been studied for the purpose of displaying flour potentialities one or more of which often remain hidden in the routine testing of experimentally milled flours of different varieties. Accordingly, when the work of the Hard Winter Wheat Laboratory was begun in 1937, one of the first tasks undertaken was a study of the response of several varieties of known commercial quality to certain ingredients used in bread baking with the purpose of ascertaining which formulas and procedures were capable of accurately characterizing and evaluating new varieties for use as bread flours. The purpose of this paper is to report some of the results secured in this study.

The literature on the development of the experimental baking test has been carefully reviewed by Brooke and Sherwood (1928). They refer to the papers of Werner (1925), Fitz (1924), Blish (1926, 1927, 1927a, and 1928) as well as others which deal with the standardization and purposes of the baking test. These papers point out how "inadequate" or lean formulas, such as listed in Cereal Laboratory Methods (1941), came into use. Markley and Bailey (1931), Geddes and McCalla (1934), and Landis and Frey (1936) have emphasized the

[1] The studies herein reported are a part of the cooperative work carried on by the Division of Cereal Crops and Diseases, Bureau of Plant Industry, Soils, and Agricultural Engineering, Agricultural Research Administration, U. S. Department of Agriculture, and the Agricultural Experiment Stations of the Great Plains Region. Published as contribution No. 109 of the Department of Milling Industry, Kansas Agricultural Experiment Station.

[2] Associate Chemist and Chemist, formerly stationed at the Hard Winter Wheat Quality Laboratory, Bureau of Plant Industry, Soils, and Agricultural Engineering, U. S. Department of Agriculture, Kansas Agricultural Experiment Station, Manhattan, Kansas; now at the Federal Soft Wheat Laboratory, Ohio Agricultural Experiment Station, Wooster, Ohio.

importance of supplementing these formulas to insure adequate diastatic activity.

Dunlap (1926), Working (1929), Blish and Sandstedt (1935), and Landis and Frey (1936) recognized the importance of using an optimum baking procedure in estimating the quality of flour. Treloar and Larmour (1931) concluded that loaf volumes secured with a fixed technique do not measure baking quality.

Clark (1929) stated that most methods give only a "snapshot" of a flour's baking ability, and later (1936, 1937, and 1937a) he used a commercial sponge type formula with variations in mixing and fermentation time to determine baking characteristics more accurately. Markley (1937) used similar variations in mixing and fermentation time and called his procedure the Latin square method. He believes that baking methods should never become crystallized and rigid.

Larmour (1940) has questioned the validity of the common opinion that hard red spring wheats are intrinsically of better quality than the hard red winters, basing his opinion in part on the early work of the Hard Winter Wheat Quality Laboratory. He attributes much of the error to inadequate baking methods, especially lack of postassium bromate or some similar acting substance, and insufficient diastase which in some cases he says "has led to quite absurd conclusions."

As a result of studies with hard winter wheat flours from the 1938 crop, Barmore, Finney, and McCluggage (1939, 1940) pointed out the value of using baking methods which employ comparatively rich formulas including 4% dried skim milk and several milligrams of potassium bromate along with optimum mixing time for each flour. The data clearly showed that with this rich, milk-containing formula it was possible to include sufficient potassium bromate to condition satisfactorily the flours with the highest bromate requirements without seriously overoxidizing those with much lower requirements. This buffering effect, pointed out at the time the data were obtained, became the subject of a special investigation by Ofelt and Larmour (1940).

On the basis of these results for the rich, milk-containing formula reported by the authors, certain studies with the same type formula were carried out by others working in the same laboratory. Larmour, Working, and Ofelt (1939), using 4 mg of potassium bromate, for the most part, and 6% milk solids, obtained a correlation coefficient of +.98 for loaf volume and flour protein with composite samples of Turkey, Kanred, and Blackhull. This work, along with the studies of Bayfield, Working, and Harris (1941), West and Bayfield (1942), and Bayfield and West (1942), furnishes considerable additional data with

the rich, milk-containing, highly bromated formula. The results of these studies were characterized, for the most part, by loaf volumes consistent with the flour protein contents, and well-developed crumb grains, thus suggesting a manifestation of the potentialities of each sample and a more correct evaluation of quality.

Materials

Pure varieties grown in field plots as a part of the Cooperative Winter Wheat Improvement Program at various agricultural experiment stations and branch stations in Kansas, Nebraska, and Colorado during the five seasons 1938 to 1942 were used in these studies. These included the principal commercial varieties of hard red winter wheat, as well as a few of the more promising new ones.

Beginning with the 1939 crop, there was included each year a sample believed to represent the commercial crop of wheat grown in the area. This is referred to as a "Commercial Composite" and consisted in each case of a thorough mixture of small lots of grain from each of a considerable number (6,000 to 13,000 depending on the year) of cars of country-run, dark hard and hard red winter wheat grading 1, 2, and 3 at terminal markets in the area. These were collected and supplied to the laboratory by the Federal Grain Inspectors of the Grain Products Branch, Food Production Administration, U. S. Department of Agriculture. In the studies with the 1939 crop, which were the most extensive, and for some of the later crops, there were included also the spring wheat variety Thatcher (a composite from four locations in the spring wheat belt obtained from the Northwest Crop Improvement Association), a soft red winter wheat (variety unknown) supplied by the Mennel Milling Company, Fostoria, Ohio, and a relatively low protein sample of Chiefkan winter wheat grown near Beloit, Kansas.

The experimentally grown hard winter varieties were all composites of wheat from four to six stations, the individual stations as well as the number of stations being somewhat different in different years. The method of compositing was such that all varieties were strictly comparable for any one season. All samples were milled on the Buhler experimental mill, except Thatcher and the soft red winter which were supplied as unbleached commercially milled flour.

The accession record number (C. I. No.) of the Division of Cereal Crops and Diseases and the protein content of the flour used each year are given in Table I. There is also included in this table the optimum bromate requirement and optimum mixing time as determined in connection with the baking tests to be discussed later.

TABLE I

PROTEIN CONTENT, $KBrO_3$ REQUIREMENT, AND OPTIMUM MIXING TIME OF THE FLOURS

Variety	C.I. No.	1938			1939			1940		
		Protein	Optimum $KBrO_3$	Optimum mixing time	Protein	Optimum $KBrO_3$	Optimum mixing time	Protein	Optimum $KBrO_3$	Optimum mixing time
		%	*mg*	*min*	%	*mg*	*min*	%	*mg*	*min*
Kharkof	1,442	13.6	5	1¾	15.7	5	1¾	15.8	4 to 5	2
Blackhull	6,251	13.7	5	1¾	16.1	5	2	15.4	4 to 5	2
Tenmarq	6,936	13.3	3 to 4	3¼	—	—	—	14.9	3	2¾
Cheyenne	8,885	12.7	2	5½	15.3	2 to 3	4¼	14.7	2	5
Nebred	10,094	13.4	3 to 4	4	15.7	2 to 3	3¾	15.1	3	4
Pawnee [1]	11,669	14.0	4 to 5	1¾	15.8	5	2¾	14.9	4 to 5	2
Comanche [1]	11,673	14.7	4 to 5	3½	15.7	4	3¼	15.2	3 to 4	2¾
Chiefkan	11,754	13.5	4	1½	15.2	6	1½	14.8	4	2
Thatcher	10,003	—	—	—	14.6	2	3½	14.9	2	3¾
Comm'l Comp.	—	—	—	—	13.0	4 to 5	2¼	11.8	3 to 4	2⅞
Soft red winter	—	—	—	—	8.2	1	2¼	9.0	1 to 2	3
Chiefkan	—	—	—	—	12.2	4	1¼	—	—	—

Variety	1941			1942			Average		
	Protein	Optimum $KBrO_3$	Optimum mixing time	Protein	Optimum $KBrO_3$	Optimum mixing time	Protein	Optimum $KBrO_3$	Optimum mixing time
	%	*mg*	*min*	%	*mg*	*min*	%	*mg*	*min*
Kharkof	13.5	5	1½	13.4	5	1⅞	14.4	4.9	1¾
Blackhull	13.6	5	1⅝	13.7	3 to 4	1⅞	14.5	4.6	1⅞
Tenmarq	13.5	4	2⅛	12.9	3	2½	13.7	3.4	2⅝
Cheyenne	12.9	2 to 3	3¼	13.0	2 to 3	3½	13.7	2.3	4¼
Nebred	13.6	2 to 3	2⅝	13.0	3	2¾	14.2	2.9	3⅝
Pawnee	13.4	5	1⅝	13.4	3 to 4	2	14.3	4.5	2
Comanche	14.2	3 to 4	2⅞	14.6	3	2¾	14.9	3.7	2⅞
Chiefkan	12.9	5	1⅝	13.0	4 to 5	1⅝	13.9	4.7	1⅝
Thatcher	13.8	1	3¼	13.6	1 to 2	3¾	14.2	1.6	3⅝
Comm'l Comp.	12.5	5 to 6	2½	11.7	4	2¾	12.3	4.4	2⅝
Soft red winter	—	—	—	—	—	—	8.6	1.3	2⅝
Chiefkan	—	—	—	—	—	—	12.2	4.0	1¼

[1] Data for the nearly identical sister varieties, Kawvale × Tenmarq 11750 and Oro × Tenmarq 11672, were substituted for Pawnee and Comanche in 1939.

Methods

Since various investigators, as noted above, have shown the necessity of including various ingredients such as shortening, salt, adequate amounts of sugar, etc., in the baking formula, all of these ingredients were used in all tests. Preliminary trials indicated that 0.25% malt syrup (120°L) was sufficient for the purposes of this study and it was discovered that the detrimental effects of overbromating were highly buffered by the formula containing 4% dry milk solids. The writers

have shown (1943) that different lots of yeast may vary considerably in viability. For this reason the yeast was standardized for the 1940 and all subsequent crops. Absorption was determined according to the method described by Finney (1945). As shown in a companion paper (Finney and Barmore, 1945), an optimum mixing time for each variety is considered necessary and was used throughout. The ingredients in what is referred to herein as the basic formula were: flour 100 g, sugar 6 g, salt 1.5 g, shortening 3 g, yeast 2 g, and water as needed. All doughs were fermented for 3 hours at 30°C (86°F), proofed for 55 minutes at the same temperature, and baked for 25 minutes at 221°C (430°F). Each sample was baked as a single loaf on each of 3 days by each of the formulas used, except for the 1938 crop for which duplicates were obtained on the same day by dividing the dough from 200 g. flour into two equal parts after mixing. The data presented are averages for the three loaves, except as just indicated.

Experimental Results

Data for 1939 Crop. The most extensive studies were made with the 1938 and 1939 crops. Since a more complete and diverse set of samples was available in 1939, the results for this year are presented and discussed first. Thirteen formulas were used, seven of which differed only in the amount of potassium bromate used.

The grain scores for the winter wheat varieties grown in the uniform experimental plots, for the spring variety Thatcher, the low protein soft red winter, the commercial composite, and the medium protein sample of Chiefkan (designated as number 12) are shown in Figure 1. The loaf volumes for the same are shown in Figure 2.

The results can be most clearly visualized and interpreted by first considering Figure 1 which gives the grain scores of the baked loaves. It will be noted, first, that the addition of malt syrup and potassium bromate and, to a lesser degree, of nonfat dry milk solids, singly and in combination, tends to increase the grain scores; and, second, that with 4% dry skim milk, 0.25% malt syrup, and adequate amounts of potassium bromate, all scores, except that for the soft red winter wheat, have approximately the same values at about 80 to 90. There are some differences between varieties at the higher levels of bromate, it is true, but considering the error in scoring, none of these differences are of much practical significance. The grain scores of the soft red winter were not materially changed by any of the formulas and were relatively low because the protein content was very low (8.2%) for bread flours. A coarser, heavier, less resilient crumb is to be expected.

As far as grain scores are concerned, an excess of bromate within

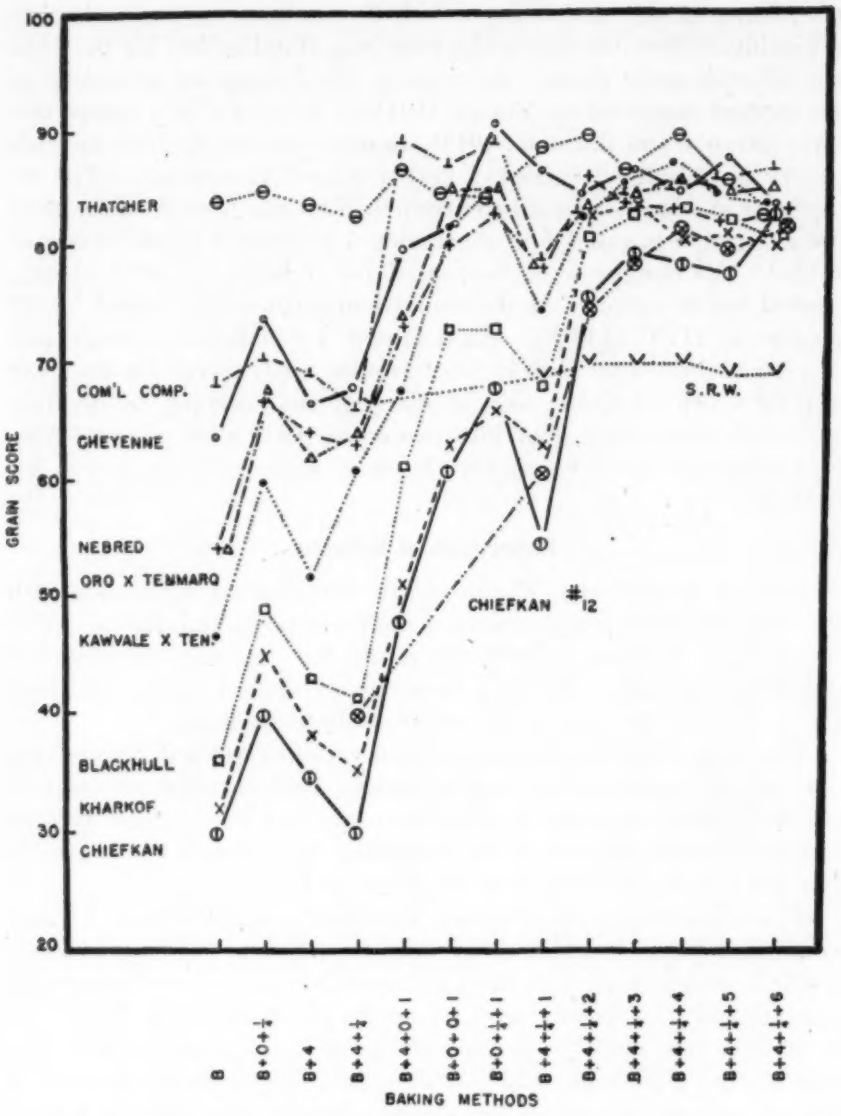

Fig. 1. Grain scores obtained with 13 baking formulas for the 1939 crop. The formulas are arranged along the abscissa in the order of average loaf volume of the varieties and complexity of formula. The formulas are indicated by the letter B (for basic) plus, first, the percentage of nonfat dry milk solids; second, the percentage of malt syrups; and, third, the milligrams of potassium bromate included. Thus, B + 4 + ½ + 1 indicates the basic formula (as used here, not the A.A.C.C. formula) plus 4 g of nonfat dry milk solids, ½ g of malt syrup 120°L, and 1 mg of potassium bromate.

the limits here used does little or no harm to any of the varieties. Both the soft red winter and Thatcher sample showed only very slight improvement when bromate was added, thus indicating a low bromate requirement. There was also very little deleterious effect resulting

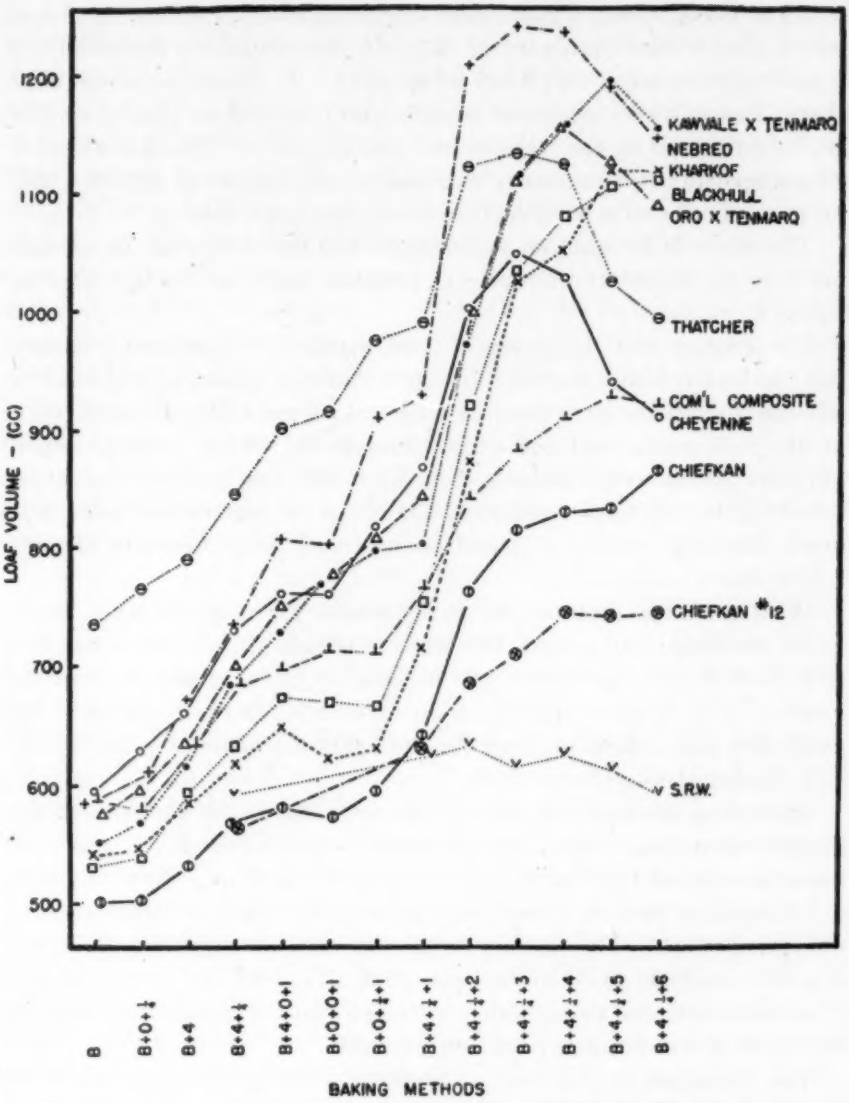

Fig. 2. Loaf volumes obtained with 13 baking formulas for the 1939 crop. See explanation under Figure 1.

from the use of the larger amounts of bromate which was far in excess of the requirements of these samples. Such results can be expected only when an adequate amount of dry skim milk (about 4% or more) is used. This buffering effect was pointed out by the authors during studies with the 1938 crop and subsequently became the subject of a special investigation by Ofelt and Larmour (1940).

The similarity of the grain scores of different varieties at the higher

bromate levels affords a reasonable degree of assurance that there was proper dough development and that the bread-making potentialities of each variety were expressed adequately. It should be noted that when all grain scores are about equally good, protein or gluten quality can be estimated on the basis of loaf volumes alone. This is a double advantage since it is necessary to consider only one set of figures which are impersonal and not subjective as are the grain scores.

The effect of formula on loaf volume and the ability of the various methods to differentiate between varieties may be readily seen in Figure 2.

Considering first the group of hard winters, it is evident not only that the loaf volumes increase, but also that the spread in loaf volume between the various varieties increases very markedly as malt, nonfat dry milk solids, and potassium bromate are added. For example, the extreme difference between the high and low volumes increases from 95 cc for the basic method to 625 cc for the method including 4% nonfat dry milk solids, $\frac{1}{4}$% malt syrup, and 3 mg bromate (B + 4 + $\frac{1}{4}$ + 3).

With the basic method the spring wheat Thatcher makes a much better showing that any of the winter wheats and is improved less when additional ingredients are supplied. It is pertinent to note, however, that it does improve quite markedly, its loaf volume with nonfat dry milk solids, malt syrup, and optimum bromate being nearly 55% greater than without them.

There is a marked difference in the response of the varieties to the different formulas. The soft red winter responds the least, again no doubt because of the low protein content of the flour. Next in order is the medium protein Chiefkan, followed by Chiefkan from the experimental plots. The protein content of the latter, as may be noted in Table I, is fully equal to the average of all others, and hence its lack of response relative to the other varieties can be interpreted only as the result of a deficiency in gluten strength.

The variation in response to bromate alone also is very marked, varying from 40 cc for the soft red winter to approximately 500 cc for Kharkof, Blackhull, Nebred, and Kawvale × Tenmarq. It is possible to use too much bromate for approximately optimum loaf volumes and the best differentiation between varieties. This is especially well illustrated by Cheyenne and Thatcher, the loaf volumes of which were decreased about 140 cc by the excess bromate used. However, because of the buffering effect of the nonfat milk solids, the amount of bromate can vary about 1 mg either way from the optimum without seriously affecting loaf volume.

The bromate requirement, *i.e.*, the amount needed to produce approximately the best loaf volume, varies considerably. It is approximately 1 mg (0 mg for all practical purposes) for the soft red winter, 2 mg for Thatcher, and 5 mg for Kharkof, Blackhull, Kawvale × Tenmarq, and about 6 mg for the experimentally grown Chiefkan. The bromate requirements would doubtless be different if an appreciably different formula and baking procedure were employed. In this study, however, two factors, at least, are related to bromate requirement and response, the variety (probably characteristic of the protein), and the protein content. Chiefkan, for example, with 15.2% protein required about 6 mg, while the medium protein samples of this same variety (12.2% protein) required only 4 mg. Also the high protein Chiefkan increased about 300 cc in loaf volume, while the medium protein sample increased only 180 cc as a result of adding bromate only to the formula. Nebred and Kharkof, two varieties grown side by side, have the same protein content and equal bromate responses but their bromate requirements are 2 to 3 mg and 5 mg, respectively. Nebred and Cheyenne, with about equal protein contents and bromate requirements, have responses of 505 cc and 320 cc respectively (a characteristic of their proteins). The markedly small requirement and response of the soft red winter are in line with its very low flour protein content.

Data for Five Years. The formulas used with the 1939 crop were also used for the 1938 crop but only those including increments of potassium bromate were used for the other crops. The data relating to bromate requirement are of special interest and are presented in Figures 3 and 4. For the 1941 and 1942 crops some of the increments of bromate were omitted since by that time it was obvious that the approximate optimum loaf volumes and dependent bromate requirements could be determined from a knowledge of protein contents, handling properties, mixing times, and the characteristics of the finished loaves. All samples were first baked with a fixed amount of 2, 3, or 4 mg of potassium bromate, depending on whether they were hard springs or hard winters. A need for appreciably more or less bromate could be detected with considerable accuracy from the outside and inside properties of the finished loaves and to some extent from the handling properties of the doughs during fermentation. It can be seen from Table I that for the samples at the high protein levels, those with short to medium mixing times almost invariably have medium to large bromate requirements, while those with medium to long mixing times have, for the most part, small to average bromate requirements. When these facts are considered along with the influence of protein

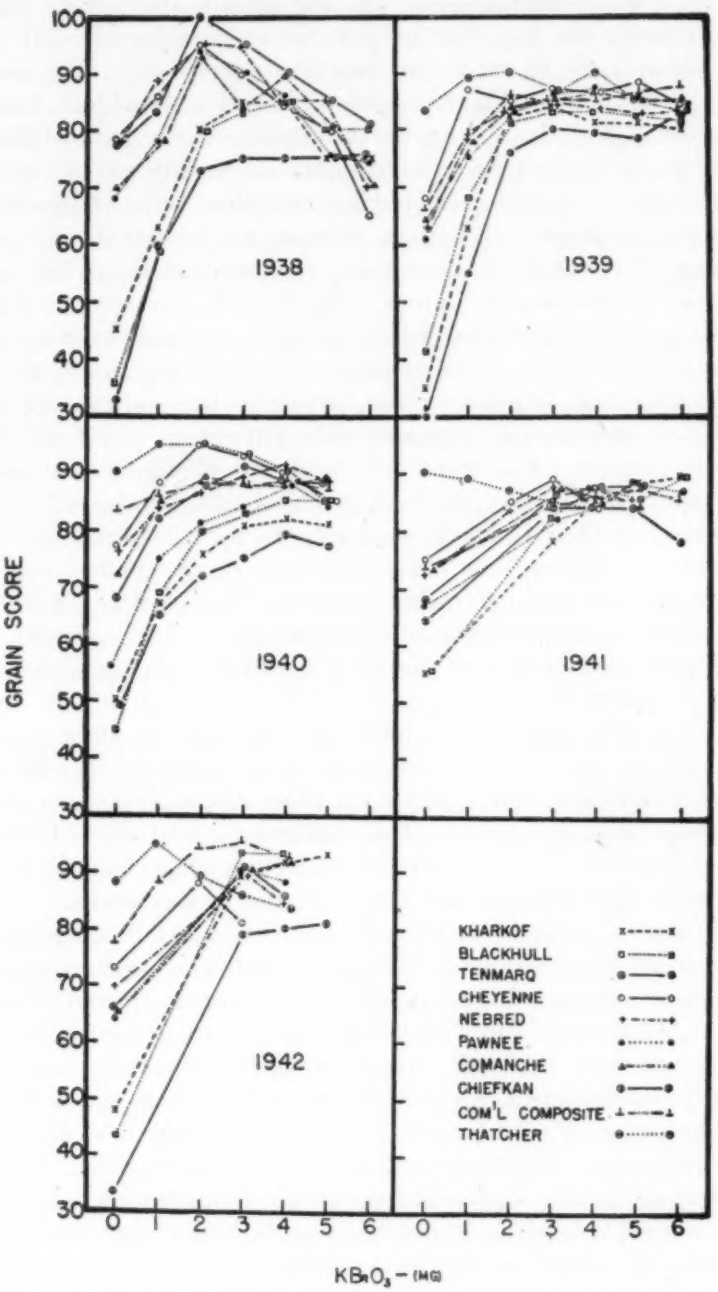

Fig. 3. Crumb grain scores for loaves baked with various levels of potassium bromate added to the rich formula (basic formula plus 4 g of nonfat dry milk solids and ½ g of malt syrup 120°L).

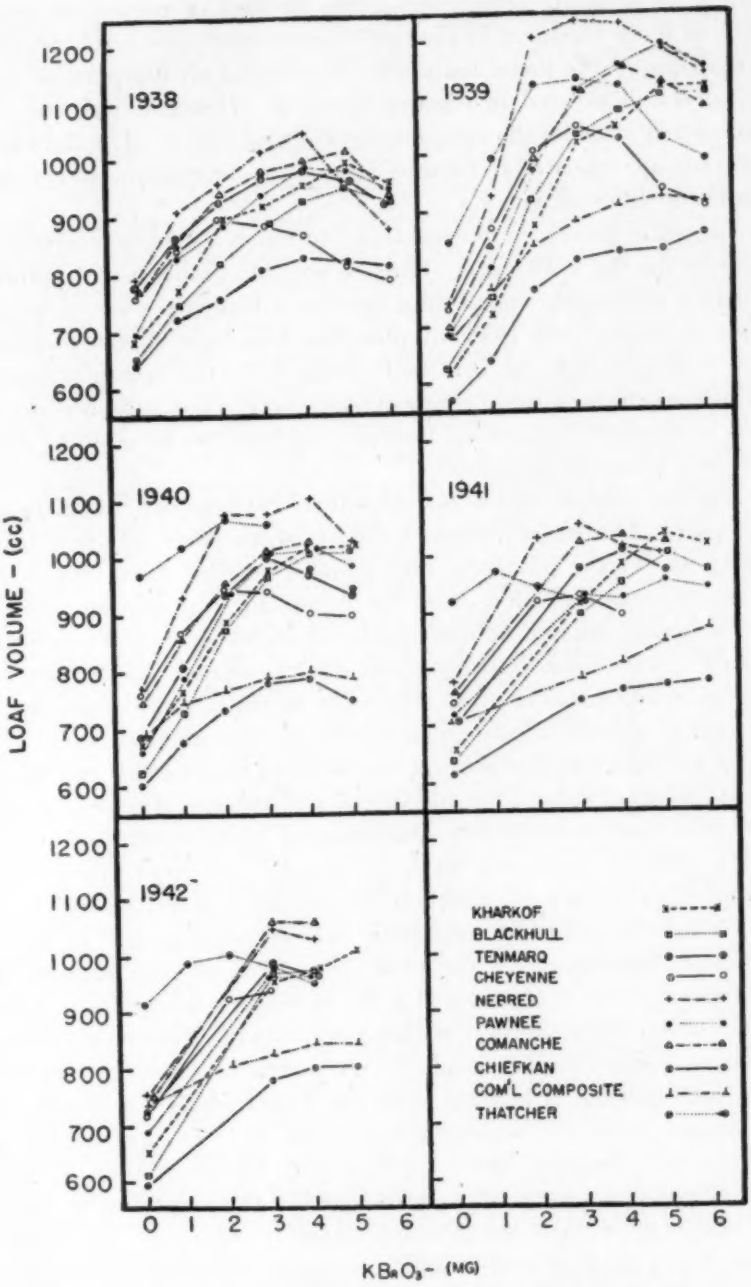

Fig. 4. Loaf volumes obtained with various levels of potassium bromate added to the rich formula (basic formula plus 4 g of nonfat dry milk solids and ½ g of malt syrup 120°L).

content on bromate requirement, the amount of potassium bromate required for subsequent bakes can be estimated sufficiently accurately so that one of the increments will give results on the plateau part of the curves illustrated in Figures 1 and 2. Hence it was considered unnecessary to bake the complete series in all cases. The data for the 1939 crop are repeated in Figures 3 and 4 for convenience in comparing results for different years.

The grain scores, in general, tend to reach a common level as was observed for the 1939 crop. The less uniform grains usually produced in loaves containing more than optimum bromate were given more weight in scoring the 1938 samples than was later shown to be justifiable. Recognition of this fact along with the use of closer roll settings resulted in more uniform grain scores for subsequent crops. Thus it appears that excess bromate reduces the score more for the 1938 crop than for the others.

The loaf volume curves for individual varieties are much the same each year. Differences between varieties are most apparent in 1939 because of (1) the relatively high protein level of most varieties and (2) the contrastingly low level for others in that season. In every case, however, the loaf volume markedly increases until a maximum is reached, after which it drops more or less sharply except for those varieties such as Chiefkan, in which the bromate requirement in some instances is approximately equal to the greatest amount used.

The bromate requirements of the different varieties for any one year and of the same variety for any one or the average of several different years may most conveniently be compared by reference to Table I.

The variation from year to year, although not great, can be in part attributed to the lack of yeast standardization and control for the 1938 and 1939 crops and to an increase in the temperature (77° to 82°F) of the baking laboratory for the 1942 crop. Taking into account these disturbing factors, it appears that the bromate requirement is a fairly stable varietal characteristic within the limits of environmental conditions and protein contents studied. It is apparent, also, that Kharkof, Blackhull, Pawnee, Chiefkan, and the Commercial Composite have the largest bromate requirements, with Nebred, Comanche, and Tenmarq intermediate and Cheyenne and Thatcher low. It should be emphasized, however, that an estimate of this requirement depends very materially on how the baking tests are made, especially as regards mixing time, amount and viability of yeast, temperature during fermentation, length of the fermentation period, and the use of adequate amounts of milk, malt, and shortening in the formula. The actual bromate requirement as reported above would not be expected to hold

for conditions materially different from those used in these studies, although the relative amounts for the different varieties probably would be maintained.

General Discussion

The data secured in this study and previously reported in the literature leave no room for reasonable doubts as to effects of bromate and certain other ingredients on baking test results. The relation of these to varietal evaluation remains to be considered. The purpose of most variety testing is to sort out the "good" and the "poor" varieties. There is, however, a difference of opinion as to how this should be accomplished. It is sometimes contended that all that is necessary is to compare all new varieties with a standard variety of acceptable quality using some simple baking formula and method which would rank highest those varieties having properties similar to those of the standard. Something could be said for this point of view if all commercially desirable and acceptable varieties had similar properties to the extent that they responded in a similar manner to a given baking procedure. This procedure overlooks or ignores a number of important considerations. One important fact often overlooked is that hard winter wheats are used in hundreds of bakeries and communities in all parts of the United States and in foreign countries in which quite different formulas and procedures are followed in producing various types of bakery products. Flours differing in such properties as protein content, bromate requirement, bromate response, mixing time, and dough handling characteristics are desired for the various products. Sometimes a winter wheat flour is used alone, but more frequently it is blended with flours from weaker wheats or the wheat is blended before milling. Varieties differing widely in the above-named properties are in large scale commercial production and in demand by different millers and bakers. These facts offer considerable assurance that no one variety or type of hard winter wheat would be satisfactory for all uses. To accept one variety or a few similar varieties as standards and hew close to the line as has been advocated might well result in discarding or condemning varieties that are really better than the standard for some bakeries or some purposes—or even for a majority of them—rather than merely discarding those varieties that are distinctly and unquestionably poor.

A sounder philosophy would seem to be one which regards the bread-baking test as first and foremost a method—at present the only satisfactory method—of evaluating protein or gluten quality. Other characteristics such as protein content, color (due to carotenoid pig-

ments), mixing time, absorption, hardness of grain, etc., can be reliably and more easily determined by other means, though of course the baking test may supply information on some of them.

If the baking test is regarded primarily as a measure of protein or gluten quality, it is obviously necessary to provide the conditions (optimum bromate, mixing time, absorption, yeast, etc.) that will assure an expression of inherent quality. None of several factors including those just named can be permitted to function in a limiting capacity. Reference to Figure 2 will readily show why the commercial value of various protein levels within hard winter wheats has not in the past been properly evaluated with most formulas containing only 1 or even 2 mg of bromate. For example, with the formula containing milk, malt, and 1 mg of potassium bromate, the high and medium protein Chiefkans and the soft red winter flour produced equal volumes in spite of the fact that they contained 15.2, 12.2, and 8.2% protein respectively. With optimum potassium bromate levels these large protein differences were logically and accurately expressed.

Both Kharkof and Blackhull (Fig. 4), in spite of their having from 1% to 4% *more protein* depending on the crop year, produced loaf volumes about equal to or less than those of the Commercial Composite when using 1 mg of potassium bromate. With about 5 mg of potassium bromate, the three are logically evaluated according to protein content. Figures 2 and 4 offer striking examples of how insufficient amounts of potassium bromate can result in an erroneous and completely illogical evaluation of varieties which are about equal in protein quality and content, *e.g.*, such varieties as Kharkof, Blackhull, and Kawvale × Tenmarq (Pawnee in Fig. 4) appear to be far inferior to Thatcher with the B + 4 + ¼ + 1 formula. With bromate levels suitable for each, however, these varieties are evaluated according to the opinion of the trade so far as can be learned.

Another striking comparison includes Cheyenne which with 1 mg of bromate is definitely superior to Kharkof and Blackhull. The latter varieties require more bromate, however, and when supplied adequate amounts as in the B + 4 + ¼ + 4, 5, 6 mg bakes, they yield loaves larger than the largest attained by Cheyenne. The Kharkof used in these studies is merely a later introduction of Turkey which is generally regarded as a suitable standard of quality for hard red winter wheats. Its protein quality is equal to that for the Turkey wheat generally grown.

Another way to illustrate the effect of method on variety evaluation is to rank the varieties by each method and compare the ranks. This has been done for the 1939 crop and the results are presented in Table II. In this table varieties are given the same rank if the differences

TABLE II

RANK OF VARIETIES BY DIFFERENT BAKING FORMULAS, 1939 CROP

Formula[1]	Variety									
	Kharkof	Blackhull	Oro	Cheyenne	Nebred	Oro × Ten.	Kaw. × Ten.	Chiefkan	Thatcher	Com'l Comp.
Basic	7, 8, 9	8, 9	2, 3, 4, 5, 6	2, 3, 4, 5	2, 3, 4, 5, 6	3, 4, 5, 6	7, 8	10	1	2, 3, 4, 5
Basic + 0 + ¼	8, 9	8, 9	3, 4, 5	2	3, 4, 5	3, 4, 5	6, 7	10	1	6, 7
Basic + 4	8, 9	8, 9	2, 3	3, 4	2, 3, 4	5, 6	7	10	1	5, 6
Basic + 4 + ¼	8, 9	8, 9	2, 3, 4	2, 3, 4	2, 3, 4	5, 6, 7	5, 6, 7	10	1	5, 6, 7
Basic + 4 + 0 + 1	9	8	3	4, 5	2	4, 5	6	10	1	7
Basic + 0 + 0 + 1	9	8	3, 4, 5	3, 4, 5, 6	2	3, 4, 5	3, 4, 5	10	1	7
Basic + 0 + ¼ + 1	9	8	3	4, 5	2	4, 5, 6	5, 6	10	1	7
Basic + 4 + ¼ + 1	9	7, 8	3	4	2	5	6	10	1	7, 8
Basic + 4 + ¼ + 2	8	7	3	4, 5	1	4, 5	6	10	2	9
Basic + 4 + ¼ + 3	7, 8	6, 7, 8	2	6, 7	1	4, 5	4, 5	10	3	9
Basic + 4 + ¼ + 4	7	6	2	8	1	3, 4	3, 4	10	5	9
Basic + 4 + ¼ + 5	4, 5, 6	4, 5, 6	3	8, 9	1, 2	4, 5, 6	1, 2	10	7	8, 9
Basic + 4 + ¼ + 6	3, 4, 5	3, 4, 5	3, 4, 5, 6	8, 9	1, 2	5, 6	1, 2	10	7	8, 9
Basic + 4 + ¼ + optimum	6, 7	6, 7	3	8	1	4	2	10	5	9

[1] The values following the word basic refer to the percentage of nonfat dry milk solids, the grams of malt syrup (120°L), and the milligrams of potassium bromate, respectively. Thus B + 4 + ¼ + 1 indicates the basic formula (as used here, not the A.A.C.C. formula) plus 4% of nonfat dry milk solids, ¼% of malt syrup 120°L, and 1 mg of potassium bromate.

in loaf volumes are not statistically significant. Chiefkan ranked lowest regardless of method. Any method, therefore, might be expected to detect varieties as deficient in gluten quality as this variety. However, it should be pointed out that a poor choice of method would often result in classifying such good varieties as Kharkof and Blackhull in nearly as low a quality category as Chiefkan. On the other hand, Thatcher ranked first by a number of methods but as low as seventh with some methods. Kharkof ranked as high as third and as low as ninth, Nebred as high as first and as low as third. Cheyenne takes all possible ranks from second to eighth.

The consistency of the various baking formulas in ranking two or three varieties as well as their inconsistency in ranking a majority of the varieties is to be expected from a consideration of such contrasting flour properties as bromate requirement and mixing time and the relation of such to the baking formula. For example, Figure 2 shows that the many formulas which ranked Thatcher at the top contained little or no potassium bromate. The three of the 13 formulas which ranked it poorer than third contained 4 mg or more of bromate. Thatcher was not appreciably penalized when as much as 4 mg of bromate were used in the formula. However, other varieties which were appreciably poorer than Thatcher with 3 mg or less, because of their larger bromate requirements, also gave approximately optimum results with 4 mg.

Similarly, with larger amounts of bromate, Cheyenne gave way in ranking to those varieties with greater requirements and, more important, with greater bromate responses which were finally responsible for ranking Cheyenne as low as eighth when optimum results for all varieties were compared. Nebred, with a relatively short bromate requirement, attained a sufficiently high volume with 3 or 4 mg of bromate, so that the penalization following as a result of the higher amounts of bromate was not sufficient to alter greatly its rank among the other varieties.

Other varieties such as Kawvale × Tenmarq, Kharkof, and Blackhull have high bromate requirements and accordingly are ranked high by those formulas which rank Cheyenne and Thatcher low; *e.g.*, Kawvale × Tenmarq was ranked first with 5 and 6 mg of bromate, while Thatcher was ranked seventh and Cheyenne eighth.

Although Chiefkan is ranked poorest when little or no bromate is used, it remains poorest even with larger dosages, chiefly because it is the only one of the high protein varieties having a relatively small bromate response coupled with a low loaf volume in the absence of bromate. Thus the Chiefkan line (Fig. 2) is not crossed by any of

those lines representing varieties which are heavily penalized with the larger dosages of bromate.

If because of time limitations a single baking formula only can be used as, for example, in attempts to characterize and evaluate a large number of varieties, it appears that a formula containing the basic ingredients previously indicated, along with 4% nonfat dry milk solids, 0.25% malt syrup, and 4 mg of potassium bromate, would do better than any other one formula considered here. Such varieties as Cheyenne would perhaps be slightly undervalued by this formula, as also might such varieties as Thatcher in years when the bromate requirement was appreciably less than for the 1939 crop. There is no certainty, moreover, that the range in bromate requirement for all possible varieties of hard winter wheat is represented by the eight varieties included in this study. Consequently, it would appear that evaluation based on one formula should be attempted only when no other procedure is possible, and should be regarded as a first approximation only.

The impression should not be formed that all varieties of good protein quality as indicated by optimum loaf volume should necessarily be recommended as acceptable varieties from the baking standpoint. On the contrary numerous varieties of excellent protein quality have been condemned by this laboratory because one or more of their various other flour properties such as mixing time and carotenoid content have been outside the limits represented by the major varieties constituting the hard winter wheat crop.

Summary

Flours of nine hard red winter varieties grown under comparable conditions and similar in protein content, a medium protein, poor quality hard red winter variety, a hard red spring variety, a sample representing the average hard red winter wheat crop, and a single soft red winter sample all from the 1939 crop were baked into bread by 13 formulas to compare methods of measuring the bread-making potentialities. Similar bakes were made with the 1938 crop, and those studies dealing with the reaction of potassium bromate were conducted for an additional three years—1940, 1941, and 1942.

The data indicated that a formula for testing varieties of hard winter wheats should contain adequate amounts of milk, malt, and potassium bromate; that milk solids buffer the oxidative effects of bromate and also serve to buffer the detrimental effects resulting from overdosages; that varieties differ in bromate requirement and response; and that with such formulas commercial varieties are evaluated in

agreement with trade opinion. The most generally satisfactory formula was one containing 6% sugar, 1.5% salt, 3% shortening, 2% yeast, 4% nonfat dry milk solids, 0.25% malt syrup (120°L), and 2 to 6 mg of potassium bromate according to the bromate requirement of each individual variety. An optimum mixing time for each variety is considered essential, as shown by Finney and Barmore (1945).

An important feature in the use of such rich, highly bromated formulas is the tendency for all varieties to produce bread having equally good crumb structure and hence scoring alike as to grain but differing in loaf volume according to the protein content and protein quality of each variety. Thus, for varieties having the same protein content, loaf volume tends to be the sole measure of protein quality. In addition, variety differentiation is at a maximum.

For most varieties of hard winter wheat, loaf volumes increase rapidly at first and then more slowly with increasing amounts of potassium bromate until the optimum is reached, after which there is a decline. A variation of 1 mg either way from the optimum when using the rich formula is not likely to result in serious discrepancies.

If because of time or other limitations (as when testing a large number of new varieties or selections) a single bake only can be made, it appears that 4 mg of bromate will give the most reliable results when used with the formula specified above and with fermentation times, fermentation temperatures, room temperature, etc., like those used in this study. Since bromate requirement is more or less related to each of these factors, any variation in them would be expected to call for changes in the amount of bromate required for optimum results.

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OPTIMUM VS. FIXED MIXING TIME AT VARIOUS POTASSIUM BROMATE LEVELS IN EXPERIMENTAL BREAD BAKING [1]

K. F. FINNEY and M. A. BARMORE [2]

(Presented at the Annual Meeting, May 1941; received for publication June 28, 1944)

It seems to be generally agreed that an optimum mixing time for each kind of flour is necessary for commercial bread production. The optimum mixing time for hard winter wheat varies considerably according to variety. Hence, in making bread-baking tests of these varieties, it would seem necessary either (1) to use a mixing time suitable for each or (2) to show that differences in mixing time are not related in any important way to the final results, in which case a fixed mixing time would be justified. Since earlier investigations have shown that mixing the dough seems to produce effects similar to those due to oxidizers, the mixing studies were performed at several bromate levels. The purpose of this paper is to present experimental data secured in the Hard Winter Wheat Quality Laboratory bearing on this question.

Merritt and Blish (1931), Merritt, Blish, and Sandstedt (1932), and Weaver and Fifield (1935) reported an improvement in loaf volume and in grain and texture as mixing time was increased above the minimum required for uniform incorporation of the ingredients and to produce what was considered an optimum condition of the dough. Swanson and Working (1933), Clark (1936, 1937), Bohn and Bailey (1936), Baker and Mize (1937), and Freilich and Frey (1939) reported detrimental effects when the mixing was longer than necessary to develop the dough properly. Stamberg and Bailey (1938) secured the best quality bread when the dough was mixed to the point of minimum mobility as shown on the farinograph, thus indicating that both undermixing and overmixing are detrimental. Barmore, Finney, and McCluggage (1941, 1942) showed that the use of an optimum or variable mixing time in variety test baking gave a greater loaf volume differentiation between varieties and apparently a more nearly true evaluation of inherent quality. In the latter paper, lower loaf volumes were always obtained if the dough was either under- or overmixed, and the amount of decrease in volume was proportional to the amount

[1] The studies herein reported are a part of the cooperative work carried on by the Division of Cereal Crops and Diseases, Bureau of Plant Industry, Soils, and Agricultural Engineering, U. S. Department of Agriculture, and the Agricultural Experiment Stations of the Great Plains Region. Published as contribution No. 108 of the Department of Milling Industry, Kansas Agricultural Experiment Station.

[2] Associate Chemist and Chemist, formerly stationed at the Hard Winter Wheat Quality Laboratory, Bureau of Plant Industry, Soils, and Agricultural Engineering, U. S. Department of Agriculture, Kansas Agricultural Experiment Station, Manhattan, Kansas; now at the Federal Soft Wheat Laboratory, Ohio Agricultural Experiment Station, Wooster, Ohio.

of over- or undermixing. Other workers, including Clark (1937) and Markley (1937, 1939), have suggested the importance of varying the mixing time according to a flour's requirements. That the mixing requirements of hard winter wheats vary considerably has been emphasized by many workers including Swanson and Working (1933), Larmour (1940), Swanson (1941), Ofelt and Sandstedt (1941), Johnson and Swanson (1942), and Barmore, Finney, and McCluggage (1941, 1942).

It has been pointed out by several workers, including Swanson and Working (1933), Aitken and Geddes (1934), Bohn and Bailey (1936), Baker and Mize (1937), Freilich and Frey (1939a), Munz and Brabender (1940), and Baker, Parker, and Mize (1942), that mixing the dough seems to produce effects similar to those due to fermentation and oxidizers. These three factors, however, are by no means completely interchangeable.

Materials and Methods

The work reported here was conducted with varieties of hard winter wheat grown in the Cooperative Winter Wheat Improvement Program and with one variety of spring wheat, Thatcher, as described in a companion paper dealing with baking methods (Finney and Barmore, 1945). Preliminary studies were carried out with the 1938 and 1939 crops, and the principal study, the results of which are reported in this paper, was conducted on the 1940 crop. The flours of the 1940 crop were a part of the same lots used for the study of baking methods by Finney and Barmore (1945). The rich formula including 4% nonfat milk solids, ¼% 120°L malt syrup, 6% sugar, 1½% salt, 3% shortening, and 2% yeast was used in all bakes. Bakes were made without potassium bromate and with various amounts in order to determine the relation between mixing time and bromate level. The optimum mixing time was determined by the appearance and feel of the dough. It is defined in this study as the time in minutes required to incorporate the ingredients and develop a smooth, elastic dough that is not sticky from overmixing. Replicate determinations usually agreed within the limits of $\pm \frac{1}{8}$ minute. All loaf volume data presented are averages of at least three replications.

Experimental Results

Mixing Time and Potassium Bromate. In the preliminary studies with the 1938 crop, undermixing reduced the quality of bread in proportion to the degree of undermixing, but overmixing did not affect the quality. It is pertinent to point out that not more than 1 mg of potassium bromate was used, which amount is now known to

be inadequate. These somewhat confusing results obtained in overmixing are explained by the later results for the 1940 crop. Various amounts of bromate were used with the 1939 crop to determine whether the effects of potassium bromate and mixing time are interchangeable. It was found that they are not completely so, since, regardless of the amount of bromate used with a fixed mixing time, over- and undermixing of the doughs could not be completely compensated for. Also the differences between the loaf volumes for the optimum mixing time and the constant mixing time doughs became progressively greater with the amount of under- or overmixing. This appeared to be true even when the amount of potassium bromate used was the optimum for each type of mixing.

To investigate the preliminary observations more thoroughly, flours of the nine varieties of the 1940 crop were baked without potassium bromate and with all increments of bromate from 1 to 5 mg with an optimum mixing time for each variety and also with a 2-minute and a 5-minute fixed mixing time. The resulting loaf volumes and grain scores are shown in Figures 1 and 2. The varieties are given at the top of each set of two curves with the optimum mixing time. Milligrams of bromate used for each variety are indicated along the bottom. Loaf volumes and grain scores are indicated on the ordinates.

The comparison of the optimum mixing time and a 2-minute fixed mixing time (top of Figures 1 and 2) is limited to five varieties because the optimum mixing time of the other four is 2 minutes or the same as the fixed mixing time used for the five varieties. For a similar reason the 5-minute fixed mixing time (center and bottom of Figures 1 and 2) is compared with the optimum mixing time for only eight of the varieties.

The arrangement of the graphs is such that, for all varieties in the upper one third of Figures 1 and 2, a fixed mixing time (2 minutes) represents undermixing, the amount of which was small for some varieties and considerable for others, depending on the optimum mixing time for each. On the other hand, for the varieties in the center and lower one third of the graphs, a fixed mixing time (5 minutes) represents overmixing, the amount of which again depended on the optimum mixing time of each.

For three of the varieties, Tenmarq, Cheyenne, and Comanche, the bromate requirement (*i.e.*, the amount of bromate used to secure the greatest loaf volume) was slightly higher (about 1 mg) when the dough was undermixed (2 minutes) than when the optimum mixing time for each was used. For Nebred there was no difference, and for Thatcher less bromate was required for the 2-minute mix than for the optimum mix, which for this variety is 4 minutes. Overmixing, on

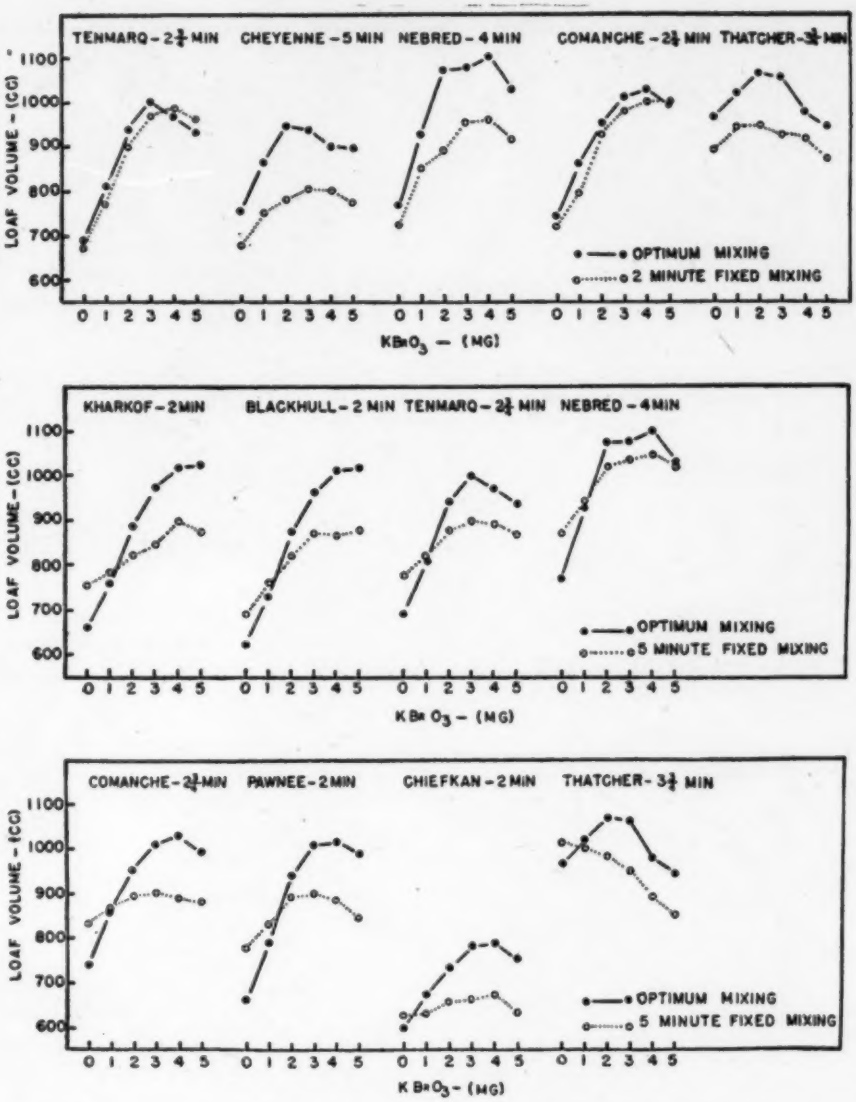

Fig. 1. Loaf volumes obtained in a comparison of optimum (shown after variety name) and two fixed mixing times using various amounts of potassium bromate.

the other hand, reduced the bromate requirement for Blackhull and Pawnee about 1 mg and for Comanche and Thatcher about 2 mg but had little or no effect on the bromate requirement of Kharkof, Tenmarq, and Chiefkan. Considered from a slightly different point of view, the longer mixing (optimum mixing time for the top one third and the 5-minute mixing time for the lower two thirds of Figure 1) in all cases produced larger loaves when no bromate was used and

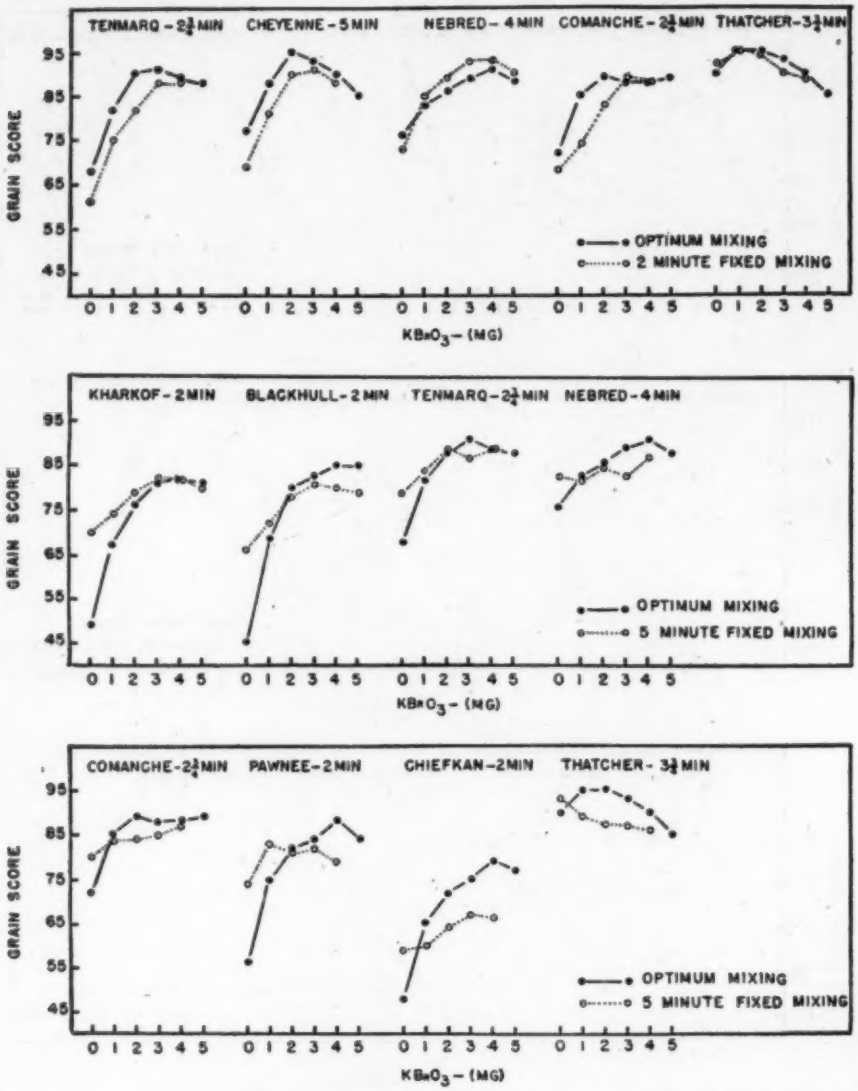

Fig. 2. Grain scores obtained in a comparison of optimum (shown after variety name) and two fixed mixing times using various amounts of potassium bromate.

generally so when only 1 mg was used. These results are consistent with those obtained for the 1938 crop and show beyond reasonable doubt that mixing compensates to a large degree for a lack of potassium bromate and vice versa when not more than 1 mg of bromate is used.

A more important fact is that, in the presence of more than 1 mg of potassium bromate, additional mixing cannot compensate for lack of bromate and, conversely, additions of bromate do not compensate

for inadequate mixing. That is, both an optimum bromate level and an optimum mixing time are necessary for best results. This perhaps can be most clearly seen by comparing the general level of the loaf volume curves secured by optimum mixing time with those secured with a fixed mixing time, considering especially those portions of the curves representing optimum or near optimum levels of potassium bromate, at which levels the loaf volumes are higher for the optimum mixing times in all cases. Furthermore, the differences increase, in general, with the degree of under- or overmixing.

Thus the 2-minute fixed mixing time for Tenmarq and Comanche (upper one third of Figure 1) produced practically as good bread as the optimum mixing time, for the obvious reason that the fixed mixing time was nearly the same as the optimum ($2\frac{3}{4}$ minutes) for these varieties. The differences for Nebred and Thatcher (the lower two thirds of Figure 1) are somewhat greater. In these instances the optimum mixing time (4 minutes) was 1 minute less than the fixed mixing time that was used. On the other hand, the loaf volume differences for Cheyenne, Nebred, and Thatcher with a fixed mixing time of 2 minutes and for Kharkof, Blackhull, Tenmarq, Comanche, Pawnee, and Chiefkan with a fixed mixing time of 5 minutes are large, as also are the differences between the optimum and the fixed mixing times.

The grain scores of Figure 2, in general, are in accord with the loaf volumes shown in Figure 1. That is, grain scores tended to be improved by whatever treatments increased the loaf volumes. The degree of improvement was not always the same, but the differences as compared with loaf volumes appear for the most part to be within the limits of experimental errors.

The effect of the amount of over- and undermixing on loaf volume can perhaps best be seen in Table I and Figure 3 in which the varieties are arranged in the order of their mixing requirements. The volume comparisons are made at the bromate levels which are optimum for the optimum mixing times.

It will be seen that the differences for the optimum and 2-minute mixing time increased from 0 cc for those varieties that were not undermixed to 167 cc for Cheyenne which was undermixed 3 minutes. Likewise with the 5-minute fixed mixing time the differences increased from 0 cc for Cheyenne, which was neither over- nor undermixed, to 152 cc for Kharkof which was overmixed 3 minutes. Similarly the loaf volumes of Blackhull and Pawnee were decreased to the extent of 137 cc and 131 cc, respectively, by 3 minutes' overmixing. A somewhat smaller decrease, when overmixing Chiefkan to the same extent, is to be expected because of its lower volume level. Figure 3

TABLE I [1]

OPTIMUM LOAF VOLUMES OBTAINED FOR OPTIMUM, TWO-MINUTE, AND FIVE-MINUTE MIXING OF DOUGH

Variety	Optimum mixing time	Loaf volume				
		Optimum mixing	2-min mixing	5-min mixing	Diff. between opt. and 2-min mixing	Diff. between opt. and 5-min mixing
	min	*cc*	*cc*	*cc*	*cc*	*cc*
Kharkof	2	1,023	1,023	871	0[2]	152
Blackhull	2	1,015	1,015	878	0[2]	137
Pawnee	2	1,016	1,016	885	0[2]	131
Chiefkan	2	785	785	672	0[2]	113
Comanche	2¾	1,028	1,000	890	28	138
Tenmarq	2¾	1,002	965	896	37	106
Thatcher	3¾	1,068	947	985	121	83
Nebred	4	1,103	963	1,048	140	55
Cheyenne	5	945	778	945	167	0[2]

[1] See Table I Finney and Barmore (1945) for protein content and optimum potassium bromate requirement.
[2] The optimum and fixed mixing times are equal.

clearly shows that, in general, the loaf volume decrease becomes greater as the amount of over- or undermixing increases.

Mixing Time and Dough Temperature. In the preliminary studies with the 1939 crop the temperatures of the doughs at the end of the mixing periods were recorded. In these studies a 4-minute fixed mixing time was used for comparison with the optimum. The results

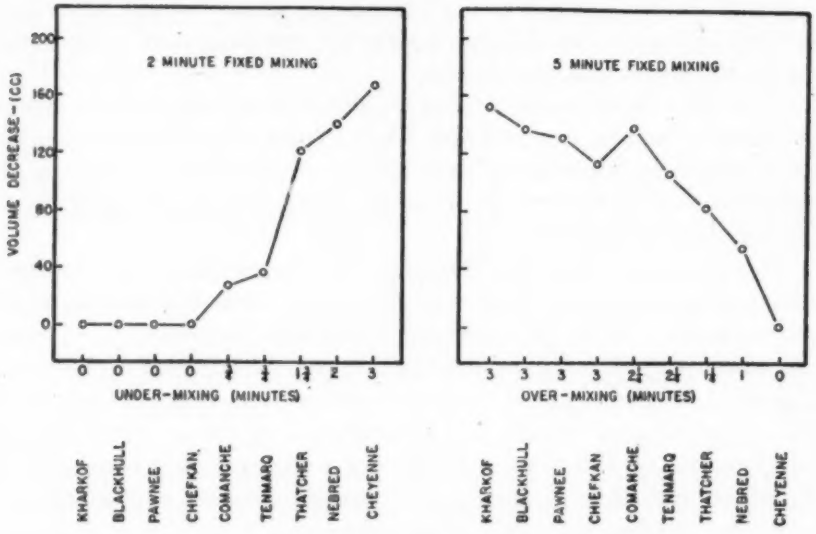

Fig. 3. Loaf volume decreases resulting from various degrees of under- and overmixing from the optimum.

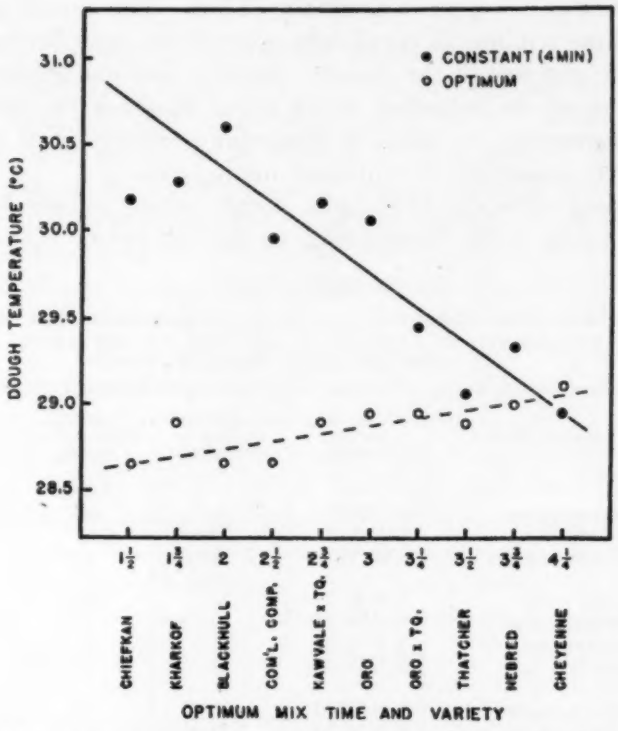

Fig. 4. Dough temperatures resulting from fixed and optimum mixing.

are presented graphically in Figure 4. In this figure the varieties are arranged along the abscissa in the order of their optimum mixing times.

With an optimum mixing time for each variety, the temperatures for all doughs just out of the mixer were the same within about 0.4°C for a difference of nearly 3 minutes in optimum mixing time. The tendency for the dough temperature to increase as the optimum mixing time increases is probably due to a tendency to undermix those varieties which develop and break down rapidly, and overmix those with opposite properties. With the fixed mixing time of 4 minutes the dough temperatures markedly increase as the optimum mixing time decreases or the amount of overmixing increases. This increase is as much as 1.7° to 2.2°C for such varieties as Chiefkan, Kharkof, and Blackhull which are overmixed the most. These data suggest that the fixed mixing technique does not treat all flours the same. With an optimum mixing time the same amount of heat is dissipated in all doughs regardless of their relative rates of, or times required for, hydration. These data suggest that optimum mixing fundamentally treats all flours the same, producing a comparable structural condition in the dough, while a fixed mixing time results in a variable dough condition.

Determining the Optimum Mixing Time. The optimum mixing time in these studies, as previously pointed out, was determined by appearance and feel of the dough. Another and less subjective way is by means of the recording dough mixer in which the peak of the curve representing the point of minimum mobility or of maximum resistance is considered the optimum mixing time.

Beginning with the 1938 crop, dough mixing curves have been made for many of the flours baked in this laboratory. The original

TABLE II

CORRELATION COEFFICIENTS FOR OPTIMUM MIXING TIME AS DETERMINED BY APPEARANCE AND FEEL OF THE DOUGH AND FROM RECORDING MIXER CURVES

Groups of samples studied	Type of recording mixer	Number of samples in each group	Speed of nonrecording mixer	Corr. Coef.
			RPM	*r*
1938 Uniform plots	O.S.W.[1]	26	66	.93
1938 Individuals	S.W.M.[2]	27	66	.98
1938 Uniform nursery	S.W.M.	30	66	.93
1939 Protein series	N.S.W.M.[3]	33	96	.95
1939 Uniform nursery	N.S.W.M.	30	66	.96
1939 Uniform plots	N.S.W.M.	29	66	.96
1939 Specials	N.S.W.M.	18	66	.96
1940 Uniform nursery	N.S.W.M.	30	96	.96
1940 Uniform plots	N.S.W.M.	22	96	.97
1940 Specials No. 1 group	N.S.W.M.	15	96	.98
1940 Specials No. 2 group	N.S.W.M.	30	96	.95
1940 Protein series	N.S.W.M.	40	96	.96
1941 Specials No. 1 group	N.S.W.M.	22	96	.97
1941 Uniform plots	N.S.W.M.	26	96	.94
1941 Uniform nursery	N.S.W.M.	30	96	.93
1941 Specials No. 2 group	N.S.W.M.	30	96	.91

[1] Original Swanson-Working recording mixer operated at 37 RPM.
[2] Swanson-Working recording micromixer operated at 60 RPM.
[3] National-Swanson-Working recording micromixer operated at 88 RPM.

Swanson-Working recording mixer operated at 37 RPM was used for a part of the 1938 crop. The Swanson-Working recording micromixer operated at 60 RPM was used for the remainder of the 1938 crop. For the 1939, 1940, and 1941 crops the National Swanson-Working recording micromixer operated at 88 RPM was used. The correlation coefficients for the optimum mixing time as determined by the appearance and feel of the dough, and with the various recording dough mixers, were calculated and are given in Table II.

The coefficients are sufficiently high ($r = 0.91$ to $r = 0.98$) to justify the conclusion that the mixing time can be satisfactorily determined by either method.

Summary

The effect of mixing time on loaf volume and grain score of bread has been determined for several varieties of hard red winter wheat and one variety of hard red spring wheat for each of three years with several levels of potassium bromate. The results show that mixing time and potassium bromate compensate for each other to some extent but are by no means completely interchangeable. With inadequate bromate, overmixing improved the bread, probably because the deleterious effects of overmixing are more than offset by the beneficial effects of the oxidation induced by the additional mixing. With optimum or near optimum bromate levels either undermixing or overmixing reduced the loaf volumes and crumb scores, the decrease being proportional to the departure from the optimum mixing time.

The data afford a satisfactory explanation of the conflicting results previously reported for overmixed dough. It appears to be clearly demonstrated that overmixing produces a deleterious effect, but if the dough is not sufficiently oxidized these effects may be obscured by the beneficial effects of the additional oxidation provided by the longer mixing time. Undermixing irrespective of oxidation produces lower loaf volumes and poorer bread than a flour is capable of producing. These relations appear to be especially important in work designed to characterize and evaluate varieties of hard red winter wheat which vary a great deal with respect to mixing and bromate requirements.

When an optimum mixing time was used, all doughs came out of the mixer at approximately the same temperature. Overmixing increased the temperature of the dough, the increase being proportional to the degree of overmixing.

Correlation coefficients for mixing time determined by the appearance and handling properties of the dough and by the recording mixer curves for 16 different sets of material comprising a total of 438 samples ranged from .91 to .98, all very highly significant statistically, showing that optimum mixing time can be accurately estimated by the recording mixer.

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AN INVESTIGATION OF SHORTER BREAD SPONGES

HARRY C. JOHNSON [1]

Montana Flour Mills Company, Cleveland, Ohio

(Presented at the Annual Meeting, May 1944; received for publication May 26, 1944)

The cabinet method of sponge fermentation in the bakeshop is claimed to result in the use of shorter sponges. Briefly, the method consists of providing a low-ceilinged cabinet to house all of the troughs. Usually the cabinet has a series of doors on the front, just large enough to permit a trough to be pushed inside; the top of the cabinet is only high enough to clear the troughs. The cabinets are built with and without partitions between the troughs. Thus, a space is created whereby the atmosphere can be restricted and the carbon dioxide produced from the fermenting sponge held within the cabinet. The composition of the atmosphere above the sponge is therefore different from that present in the average fermentation room.

The present investigation was undertaken to study the effect of varying the composition of the atmosphere on the sponge, dough, and bread.

Materials and Methods

An attempt has been made to simulate as closely as possible the baker's methods of baking. A bleached spring wheat flour of 0.45% ash, 13.0% protein, and gassing power of 420 mm/10 g flour for 4 hours was used. The flour was stored under conditions where the moisture remained at 13.5 to 14.0%. The baking formula used is shown in Table I.

The mixer was a Hobart C–10 with McDuffee bowl and fork attachment, and water jacket to compensate for temperature changes. A double sponge was mixed as a matter of convenience and divided immediately. The doughs scaled 20.8 oz (590 g) and were baked in $4\frac{1}{2} \times 11 \times 2\frac{3}{4}''$ pans. A floor time of 10 to 15 minutes was given. The rounding and molding were done by hand, with a rest period of about 8 to 10 minutes between these operations.

Sponge fermentations were carried on in a Despatch Bailey Cabinet at 86°F (30°C). The proofing was at 100°F (37.8°C) in air. The fermentation cabinet was equipped with an inlet tube set into the wall through which it was possible to introduce various gases at will. Another tube was inserted through the side of the cabinet from which samples of the inside atmosphere could be withdrawn as desired. This made it possible to take samples without opening the doors and without

[1] Present address, Montana Flour Mills Company, Great Falls, Montana.

TABLE I

THE SPONGE DOUGH FORMULA

	Sponge [1]	Dough [2]	Total flour basis
	g	g	%
Flour	212.0	113.0	100.0
Water	125.0	100.0	69.0
Yeast	6.5	—	2.0
Yeast food	1.6	—	0.5
Salt	—	6.5	2.0
Sugar	—	9.75	3.0
Nonfat milk solids	—	9.75	3.0
Shortening	—	9.75	3.0

[1] The sponge was mixed 2 minutes in low speed at 78°F. The sponge temperature back to the mixer was 86°F.
[2] The dough was mixed in second speed for 3 to 3½ minutes at 80° to 82°F.

altering the concentration of gases existing in the cabinet while the sponges were fermenting.

An Orsat gas apparatus was used to measure directly the percentage of carbon dioxide and oxygen in the atmosphere. The percentage of nitrogen was calculated by difference. Samples of the gases were pumped directly from the fermentation cabinet to the apparatus by the use of a rubber bulb. The progress of the sponges was followed by the use of glass Chidlow expansion jars.

Experimental Results

In Figure 1 is shown the effect of composition of the atmosphere on sponge height. Fermentation in an atmosphere of carbon dioxide varying from 15.5 to 25.0% increased sponge height slightly. The results obtained in an atmosphere of nitrogen and oxygen in concentrations greater than those in normal air were identical to those fermentations in normal air. The height of sponges fermented under 5-lb air pressure was definitely decreased. From these results it is apparent that differences in composition of the atmosphere, brought about by varying the percentages of oxygen, nitrogen, and carbon dioxide, did not affect the height of the sponges to any degree.

Table II shows data on sponges, doughs, and bread where the sponges were fermented in atmospheres of widely varying composition. No. 1 is the control fermentation in normal air. On a 3-hour fermentation it gave a rather heavy sponge and a slightly tough dough in molding. The bread showed indications of under-age. In No. 2 the atmosphere varied from 15.5 to 25.0% in carbon dioxide, 15.5 to 14.0% in oxygen, and 69.0 to 61.0% in nitrogen. When the sponge was taken, it was immediately recognized that this sponge was different from the control. The gas pockets were finer and smaller in size. This indicated a greater number of gas cells with a more even dispersion. The

sponge was light and dry, and would break apart cleanly without stringing. The dough at molding was soft, lively, and extensible, and free from buckiness and toughness. The bread had greater oven spring and closer grain and texture than the control. In No. 3, where the nitrogen was increased and the oxygen decreased, the sponges and doughs were sticky and heavy, with the bread having open grain and coarse texture.

The atmosphere in No. 4 contained a minimum of 85.0% carbon

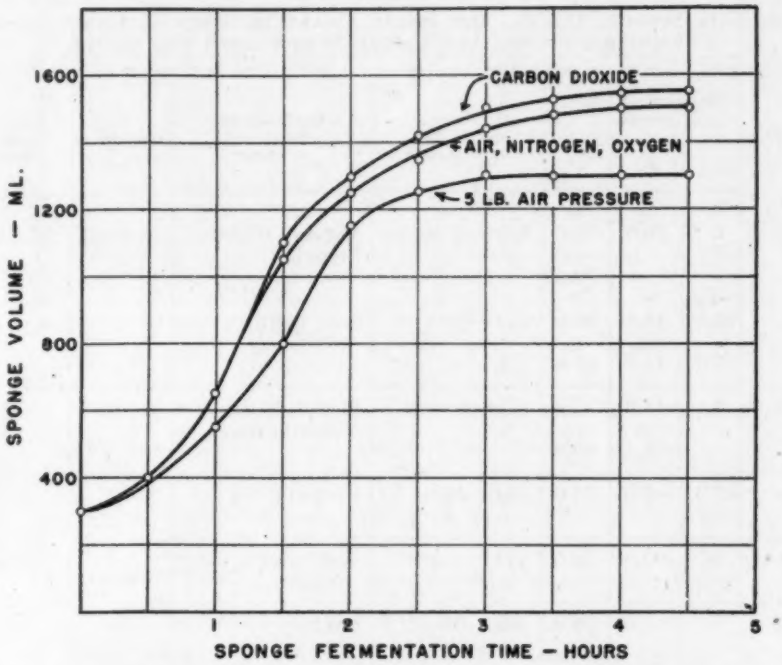

Fig. 1. Comparison of sponge volumes under atmospheres of varying composition. The top curve shows the volumes attained under an atmosphere of from 15 to 85% carbon dioxide. The middle curve shows the volumes under normal air and also under atmospheres in which the percentages of nitrogen and oxygen were varied; the nitrogen content varied from 78 to 99% and the oxygen from 20 to 90%.

dioxide which resulted in the sponges being exceedingly short and stiff, almost to the point of disintegration. The volume of the bread was less than that of the control, and the grain was open and the texture coarse.

In No. 5 a minimum of 90.0% oxygen was in contact with the sponge and it went back tough, heavy, and sticky. The dough was sticky and very bucky at molding, and the bread was poor in volume and inside characteristics.

When the nitrogen was increased to 99.0%, as shown in No. 6, the results were poorer than at 85.0% (No. 3). When the sponges were subjected to a pressure of 5 lb/sq. in. during their fermentation period

(No. 7), they were wet, heavy, and disintegrated. The doughs were tough and heavy with less than normal oven spring and the bread was open and coarse.

The only composition of the atmosphere that produced more desirable results than the control had a carbon dioxide level of 15.5 to 25.0% and an oxygen level of 14.0 to 15.5%. Under the other conditions tried, the results obtained were inferior to the control.

TABLE II

EFFECT ON SPONGE, DOUGH, AND BREAD CHARACTERISTICS OF CHANGING THE COMPOSITION OF THE ATMOSPHERE SURROUNDING THE SPONGE

No.	Atmosphere over sponge			Condition of sponge after fermentation	Condition of dough at molding	Oven spring	Grain and texture
	CO_2	O_2	N_2				
	%	%	%				
1	0	20.0	78.0 to 79.0	Normal, heavy	Normal, slightly tough	Normal	Normal
2	15.5 to 25.0	15.5 to 14.0	69.0 to 61.0	Very light, short, very dry	Soft, light, extensible	+[1]	+
3	0.1	14.0 to 14.5	83.5 to 89.0	Slightly wet	Slightly sticky, slightly tough	Normal	−[2]
4	85.0	2.0	13.0	Very short, very dry	Very stiff	−	−
5	0	90.0	10.0	Very tough, sticky	Stiff, sticky, very tough	−	−
6	0	1.0	99.0	Sticky, wet, heavy	Sticky	−	−
7	0	20.0	78.0 to 79.0	Wet, heavy, disintegrated	Tough	−	−
	5-lb. pressure/sq. in.						

[1] + Indicates positive response. [2] − Indicates negative response.

In order to approach more closely commercial cabinet conditions, the sponges were fermented in wide-mouth gallon glass jars. A $\frac{1}{4}''$ i.d. metal tube was welded into the center of each lid as a vent. After the sponge was placed in the jar, the lid was fastened tightly to exclude the outside atmosphere. During fermentation the vent was opened momentarily every 20 minutes to relieve the pressure built up. The volume of the sponge at maximum rise and the total volume of the glass jar were in the ratio of 1 : 2.

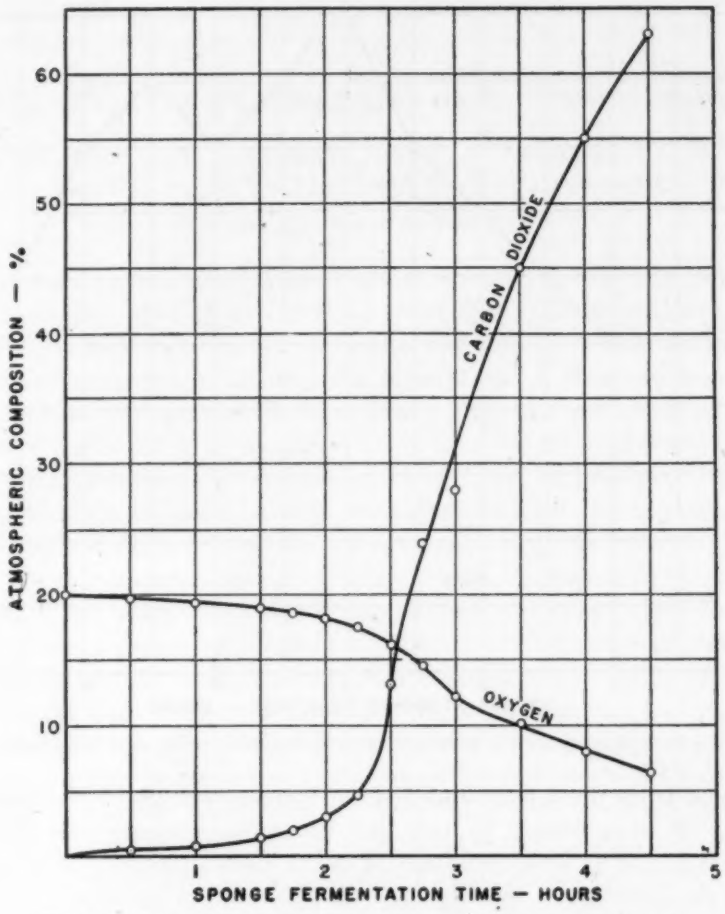

Fig. 2. Changes in the atmosphere above a sponge as fermentation proceeds.

Figure 2 shows the change in the composition of the atmosphere in the glass jars from the setting of the sponge to 4½ hours' fermentation.

During the first 1½ to 2 hours of fermentation there is a slow release of carbon dioxide from the sponge. At 2¼ to 2½ hours there is a rapid increase in the amount given off; thereafter the carbon dioxide continues to build up at a steady rate and after 4½ hours has reached 63.0%. At 6 hours as high as 85.0% carbon dioxide has been found. The percentage of oxygen varies inversely with the carbon dioxide content.

The baking results obtained from the sponges fermented in the glass jars are illustrated in Figure 3 by plotting the time in hours of the sponge against the bread score. For comparison, the scale used for scoring bread is based on the arbitrary value of 10, which was the value attained by the best loaf in the series.

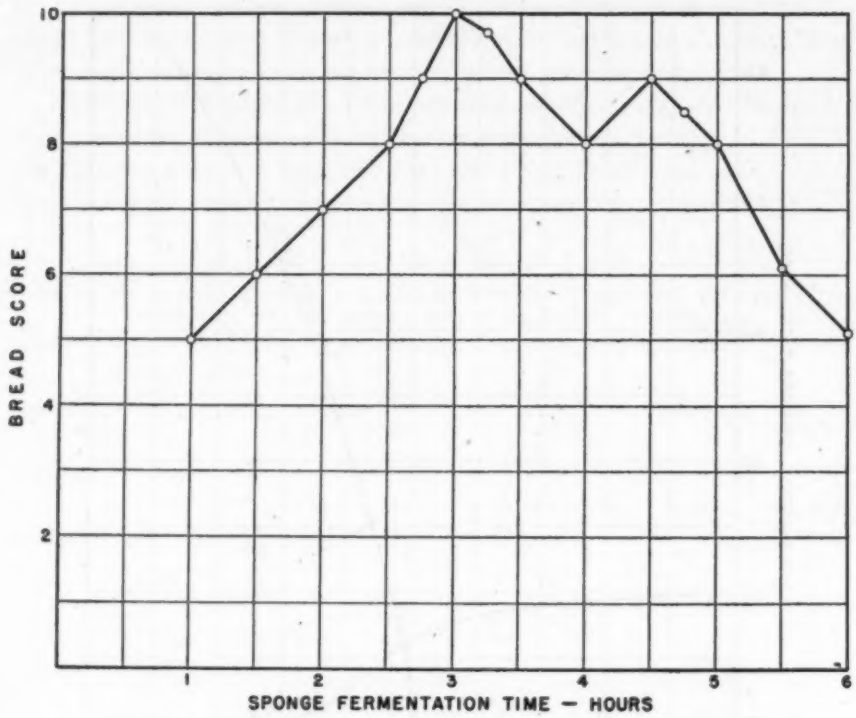

Fig. 3. Effect of sponge time on bread score when sponges were fermented in closed vessels.

Bread from the 3-hour and $3\frac{1}{4}$-hour sponges was given the highest rating. It is significant to note that the sponges whose time ranged between $3\frac{1}{2}$ and $4\frac{1}{4}$ hours produced bread of lower quality. At $4\frac{1}{2}$ to $4\frac{3}{4}$ hours, the bread score was higher. Sponge times of less than $2\frac{1}{2}$ hours or more than 5 hours produced low quality bread.

Summary

The rate of expansion and the height of sponge were not affected by variations in atmospheric concentrations of carbon dioxide, oxygen, or nitrogen. Fermenting a sponge under a pressure of 5 lb/sq. in. resulted in a slower rise and less height than when the sponge was fermented at normal atmospheric pressure. An atmosphere varying between 15.5 to 25.0% carbon dioxide, 15.5 to 14.0% oxygen, and 69.0 to 61.0% nitrogen for a 3-hour sponge produced better bread than the control fermented in normal air. Other atmospheric compositions which were tried produced bread inferior to the control.

When a closed glass jar was used to retain the carbon dioxide produced from the fermenting sponge, the highest quality bread was produced with a 3-hour sponge.

DETERMINATION OF SHELF LIFE OF PACKAGED CEREALS [1]

C. E. FELT, A. C. BUECHELE, and L. F. BORCHARDT [2]; R. C. KOEHN, F. A. COLLATZ, and F. C. HILDEBRAND [3]

(Received for publication December 4, 1944)

Consumer acceptance of ready-to-eat cereals depends in large measure upon their quality at the time of serving. These products may lose their appeal for a variety of causes, but one of the most important is loss of crispness resulting from absorption of moisture from the atmosphere. To prevent such moisture absorption, cereals are customarily packaged in containers which resist water vapor penetration. The amount of package protection which must be provided depends upon the time elapsing between manufacture and consumption, and upon the atmospheric conditions prevailing during this interval. The minimum protection required will vary with the region in which the products are stored in jobbers' warehouses and on grocers' shelves. For example, greater protection will be required for cereals destined for sale in an area of high average atmospheric water vapor pressure, such as the Gulf Coast, than in a dry region such as Salt Lake City.

The shelf life of a product in any type of package in various areas can presumably be estimated either by actual field tests or by calculation from weather data together with laboratory measurements of package efficiency under known atmospheric conditions. Of the two methods, the field test is the more direct because only two assumptions need be made; the first is that the storage location employed for the test is typical of the area which it purports to represent, and the second, that weather conditions during the test were normal for the time of year in that area. Careful selection of test locations will minimize errors arising from that source, and the fact that most field studies extend over 6 to 30 weeks will tend to lessen the effect of day-to-day weather variability. Because the storage life in a particular area is greatly influenced by the time of year in which the product is first placed in the region, the accumulation of shelf life data by actual field test in all market areas for all seasons becomes a very elaborate, expensive, and time-consuming procedure.

Shelf life data can be obtained much more readily by calculation

[1] Paper No. 62, Journal Series, General Mills Research Department, General Mills, Inc., Minneapolis, Minnesota.
[2] Research Department.
[3] Products Control Department.

from laboratory measurements of package performance plus weather data if a number of assumptions are made. The present study was designed to test whether shelf life values so calculated would agree well enough with data obtained by field test to warrant replacing all field tests with the simpler laboratory method of obtaining such data.

Field Study

Seven ounces each of a puffed corn cereal and a puffed oat cereal were packaged in cartons $6\frac{1}{2} \times 2\frac{3}{8} \times 8\frac{1}{4}''$ containing standard single waxed cereal glassine liners. The cereals were taken from commercial production, packaged under commercial conditions, and distributed to 12 different cities in the United States. They were stored, beginning in April, so as to be exposed to atmospheric conditions prevailing in commercial distribution in that area. Every two weeks, three packages of each cereal were removed at each point and sent to the laboratory by air express in special moisture-proof cartons. The packages were opened and the contents inspected for eating quality and moisture content.

The moisture content of each cereal was plotted against storage time in weeks for each city and quadratic curves were fitted to the data by the method of least squares. Past experience had enabled us to select a moisture level at which these products become unsatisfactory, and the time in weeks required for the cereals to reach this moisture level in each city was taken from the fitted curves. These values, expressive of the shelf life of each cereal in each city, are shown in Table II.

It should be emphasized that the values shown are good only for these two cereals in the particular type of package employed when storage is started during the month of April.

Determination of Shelf Life by Calculation

In estimating shelf life by calculation, the basic assumption was made that, over the range of atmospheric conditions normally encountered, the rate of water vapor gain by a packaged hygroscopic material is approximately proportional to the absolute water vapor pressure difference existing between the material and the atmosphere to which the package is exposed. This assumption has been discussed by Carson (1937) and by Halladay (1942), both of whom conclude that it holds under normal conditions but not when the relative humidity is abnormally high.

The general expression defining the amount of water vapor transmitted through a definite area of a given barrier during a definite time

interval for a given difference in water vapor pressure across the barrier is:

$$W = RAT(p_1 - p_0) \quad (1)$$

where W = weight of water transmitted;
R = permeability of the barrier in weight of moisture transmitted per unit of area per unit of time per unit of vapor pressure difference;
A = permeable area of the barrier;
T = time;
p_1 = vapor pressure of higher humidity atmosphere;
p_0 = vapor pressure of lower humidity atmosphere.

For use in this study, equation (1) was simplified by taking the unit of A to be the permeable area of the package. The rate R was then replaced by R_1, the rate per package, and the expression became:

$$W = R_1T(p_1 - p_0) \quad (2)$$

where W = water transmitted (per package);
R_1 = permeability of the fabricated package per week per unit of vapor pressure difference (pounds per square inch);
T = time in weeks;
p_1 = average water vapor pressure of the external atmosphere in pounds per square inch during time T;
p_0 = average water vapor pressure of the product in pounds per square inch during time T.

If, then, the permeability characteristics of the package, as represented by R_1, are known, as well as the vapor pressure of the atmosphere in which the package is stored and the vapor pressure of the cereal product itself, the gain of water for any definite time interval can be calculated from the equation. As has already been mentioned, the average value of the vapor pressure of the storage atmosphere can be obtained from weather bureau data.

If a given package is stored under known controlled conditions, the value of R_1 can be determined from the observed behavior of the package under these conditions. For this determination, packages were placed in a controlled weather room operating at an average temperature of 82.5°F and a vapor pressure of 0.36 lb per square inch (66% relative humidity). The rate of water vapor gain was noted by determining the moisture content of representative packages at the end of various storage periods.

Unfortunately, the calculation of R_1 is complicated by the fact that the vapor pressure of a cereal product changes with its moisture content, as shown by the curves in Figure 1. Thus, the value for p_0 in equation (2) is not a constant but is a function of W. This necessitates the calculation of R_1 by the method of progressive approximation for assigned values of R_1. By using different values of R_1 in the calculations, a value of R_1 is found that gives a moisture-time curve that closely approximates the curve obtained experimentally. The method em-

ployed in the solution for R_1 is illustrated in Table I. Here, for the sake of illustration, R_1 has been arbitrarily assigned a value of 10. At its initial moisture content of 3.35%, the corn cereal is found from moisture equilibrium studies to have a vapor pressure of 0.036 lb/sq. in.

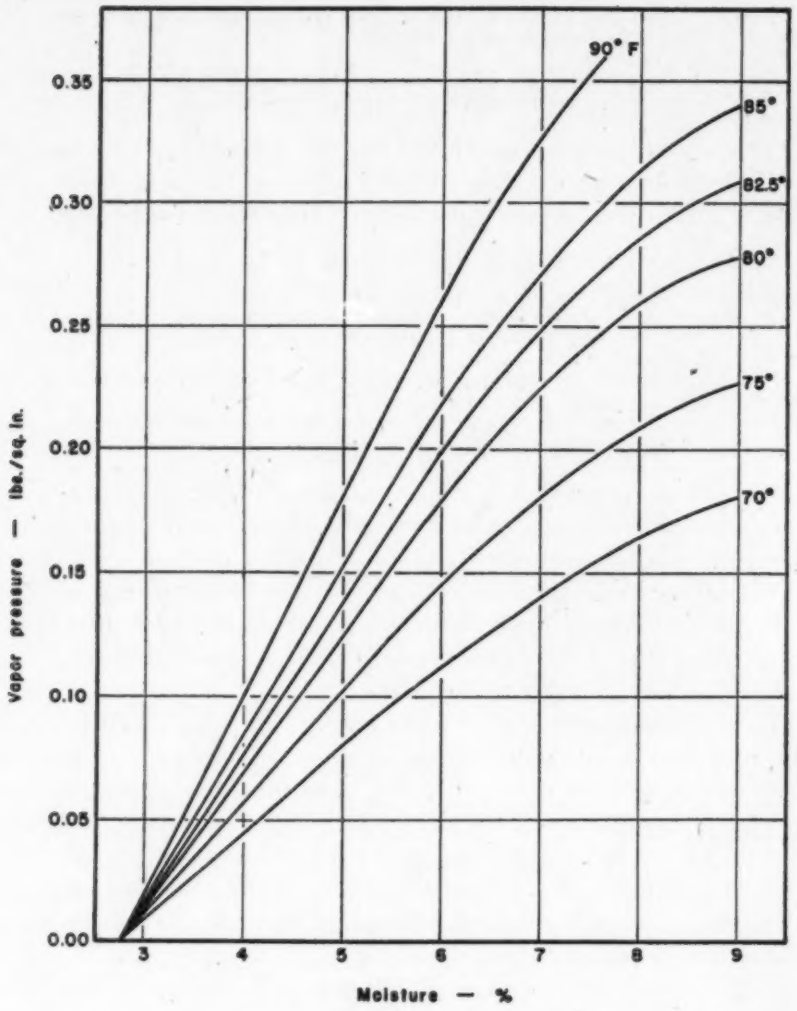

Fig. 1. The effect of moisture content on the vapor pressure of corn cereal.

It is first assumed that this cereal vapor pressure will exist throughout the first week of storage; then the vapor pressure difference between the outside and the inside of the package ($p_1 - p_0$) for this period is 0.360 − 0.036, or 0.324 lb/sq. in. For this vapor pressure difference and for the assumed value of R_1, the moisture gain would be 10×0.324.

TABLE I

ILLUSTRATION OF METHOD FOR CALCULATING INCREASE IN CEREAL MOISTURE CONTENT ON STORAGE

(Temperature 82.5°F; atmospheric vapor pressure [p_1] 0.36 lb/sq. in.; R_1 taken to be 10)

Cereal stored for	Moisture content at beginning of period	Assumed ave. v.p. of cereal during period, p_0	$p_1 - p_0$	Rate of moisture gain $W/T = 10(p_1 - p_0)$	Wt. of package contents at end of period	Moisture content at end of period
weeks	%	*lb/sq. in.*	*lb/sq. in.*	*g/week*	*g*	%
0					199.70	3.35
1	3.35	0.036	0.324	3.24	202.94	4.89
		0.084	0.276	2.76	202.46	4.67
		0.078	0.282	2.82	202.52	4.70
2	4.70	0.120	0.240	2.40	204.92	5.87
		0.154	0.206	2.06	204.58	5.66
		0.149	0.211	2.11	204.63	5.68
3	5.70					

or 3.24 g. The addition of this amount of water vapor to the cereal would bring its moisture content to 4.89% at the end of the first week of storage.

This moisture content will obviously be too high since it was calculated on the assumption that the vapor pressure of the cereal remained constant for the entire week, whereas actually it increased continuously as the moisture content increased; thus the value of $p_1 - p_0$ actually was less than that assumed in this first calculation. If, then, it is assumed that the average vapor pressure during this period was the mean of the pressures corresponding to the initial moisture, 3.35%, and the first approximation to the moisture at the end of a week's storage, 4.89%, a second approximation can be made which will more closely approach the true moisture content at the end of this storage period. This mean is the average of 0.132 and 0.036, or 0.084 lb/sq. in. The new value for $p_1 - p_0$ is then 0.360 − 0.084, or 0.276 lb/sq. in. After the calculations are repeated, it is found that this second approximation gives a moisture content of 4.67% at the end of the week of storage.

This process can be repeated as often as desired, with increasing precision in the estimate of the final moisture content. It was arbitrarily decided to discontinue each series of estimations when two successive final moisture values differed by 0.05% or less. The final value was then rounded to the nearest 0.05%.

It will be remembered that in these sample calculations a value of R_1 equal to 10 was assumed. The calculations for a given package type were repeated with various values of R_1 until a value was found for

which the calculated rate of moisture gain agreed with the rate observed when samples of this type of package were stored under known atmospheric conditions. A value of R_1 equal to 10 was found to give the best agreement for the corn cereal. (See Figure 2.) When the

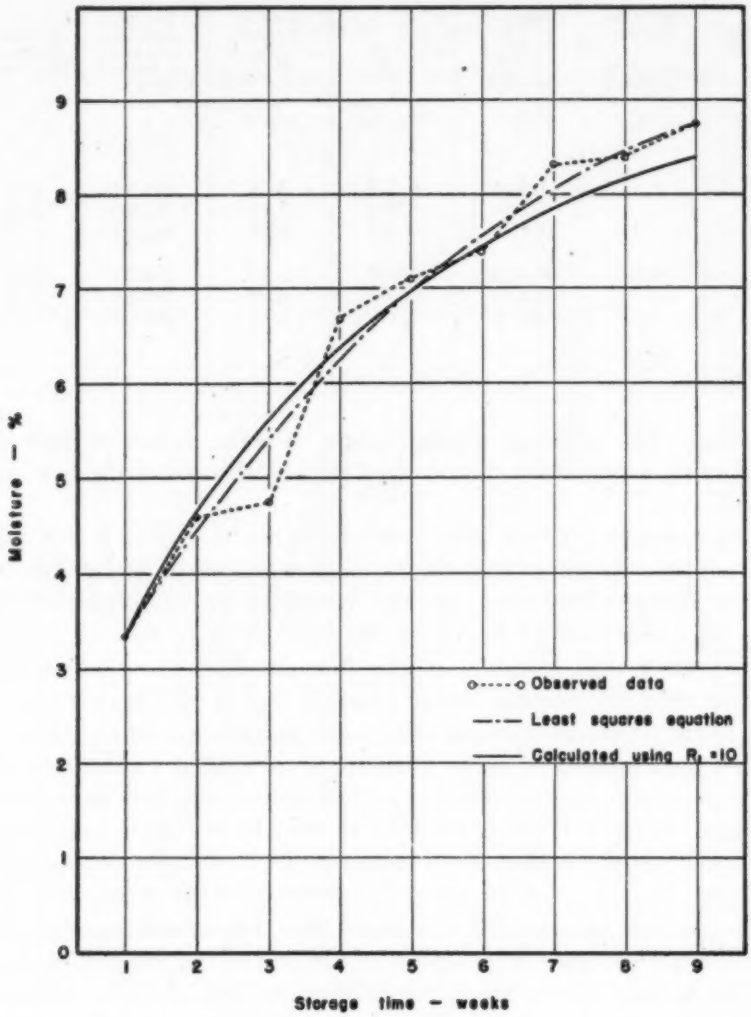

Fig. 2. Comparison of curves obtained from observed data and observed data statistically treated with curve obtained by use of R_1

factor 10 was used in the calculation for the oat cereal, the storage time found by the calculation was about 13% longer than that given by the curve obtained from experimental data by statistical means. Because, at best, approximations of the nature herein attempted are only in-

formed estimates, it was decided to use the factor 10 for both products in the following calculations. The agreement between observed and calculated results with R_1 equal to 10 is shown in Figure 2. The

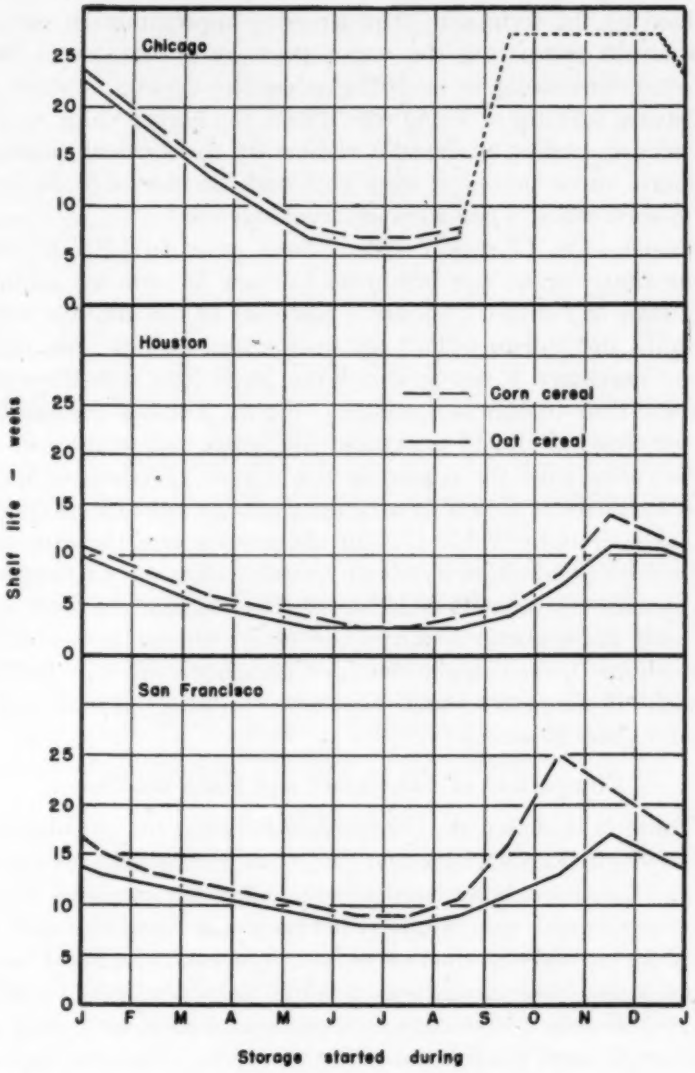

Fig. 3. Calculated shelf life of cereals in Chicago, Houston, and San Francisco.

observed data are also represented by a curve fitted to the experimental points by the method of least squares.

After the constant R_1 for any type of package had been determined in this manner, equation (2) was then employed to calculate shelf life

in 11 market areas for which weather data were available. The average vapor pressure for each month was computed from 50-year-average weather bureau figures for temperature and relative humidity in the area and these values substituted as p_1 in equation (2). The equation was solved by the technique of progressive approximation previously described. In estimating the vapor pressure of the cereal, storage temperature was taken to be 70°F, unless the average of daily mean temperatures was above 70, in which case the higher value was used. Four weeks was taken as the unit of time for these calculations unless atmospheric vapor pressures were high and the rate of moisture gain rapid; in such cases, a one-week interval was used.

For each area, 12 sets of calculations were carried out, one set assuming that storage was begun on January 15, one set assuming a starting time of February 15, etc. Each set of calculations was continued until the moisture limit for satisfactory quality was attained. The time necessary to reach this limit (shelf life) was then plotted against the time of starting storage. Figure 3 shows the results obtained for three of the 11 areas and illustrates the manner in which shelf life varies with the season of the year. Variation in shelf life between localities is shown by a comparison between the parts of this Figure, as well as by Table II. In the cases where the atmospheric vapor pressure was not high enough to cause the product to reach the critical moisture level within 26 weeks, the calculations were discontinued, and those portions of the curves are shown as broken lines. Thus in Figure 3, the calculations for Chicago storage starting during the months of August through December indicate an expected shelf life greater than 26 weeks.

Comparison of Laboratory and Field Studies

In Table II is shown the comparison between the calculated shelf life of the single liner package and that obtained by field tests starting April 15. Control cabinet results are included for comparison.

Good agreement was obtained between calculated and field study shelf life values except in the case of San Francisco. In San Francisco, the vapor pressure never reaches very high values or drops to very low values, and the effect of storage temperature on shelf life is very great, as is apparent from the following consideration. Because the rate of water vapor pickup is proportional to $p_1 - p_0$, any variation in p_0 will have a large effect on $p_1 - p_0$ if p_1 is small; and the vapor pressure of the cereal (p_0) at any moisture content increases rapidly with rising temperature. To illustrate, the value of shelf life for San Francisco is based on a storage temperature of 70°F, and a value of 11 weeks for the corn cereal was obtained by calculation. If

TABLE II

COMPARISON OF CALCULATED AND OBSERVED SHELF LIFE

(Field test started in April)

Location	Weeks to reach moisture limit			
	Corn cereal		Oat cereal	
	Observed	Calculated	Observed	Calculated
Control cabinet	5.0	5.0	3.9	4.4
Houston, Texas	4.5	5.0	4.5	4.0
Jacksonville, Fla.	5.5	6.0	4.5	5.0
Oklahoma City, Okla.	8.5	8.0	7.0	7.0
Kansas City, Mo.	10.5	8.0	9.0	8.0
Baltimore, Maryland	11.5	9.0	9.5	8.0
Chicago, Illinois	14.0	11.0	11.0	10.0
Providence, R. I.	12.5	11.0	12.5	10.0
Buffalo, N. Y.	10.0	10.0	9.5	10.0
Minneapolis, Minn.	11.0	11.0	11.0	10.0
Portland, Oregon	17.0	13.0	12.0	11.0
San Francisco, Calif.	19.0	11.0	16.5	10.0
Ogden, Utah [1]	—	—	—	—

[1] The vapor pressure in Ogden reaches a maximum of 0.15 lb/sq. in. in July and August when the mean temperature is 80°F and 75°F respectively. Under these conditions, the cereal products cannot reach the critical moisture level. This was confirmed by observation; the products on test in Ogden did not attain this level even after 24 weeks of observation.

the product had been stored at 75°F, the shelf life by calculation would have been 18 weeks. (The observed life was 19 weeks.) In almost all the other localities studied, the vapor pressure in the summer months is so high that the effect of storage temperature on shelf life is not as significant as it is in San Francisco. In Baltimore, for instance, storage at 5°F above the assumed average temperature would have lengthened the shelf life by only two weeks.

Discussion

As has already been mentioned, the quality of prepared cereals depends markedly upon the moisture content at the time of consumption. A manufacturer is faced with the question of the degree to which he must protect his product to get it to the consumer in an acceptable condition. Thus, for instance, it would be possible to package cereals of the present type in tin, under which condition the shelf life, from the moisture standpoint alone, would be indefinitely long. At the other extreme, the products could be provided with little or no protection against the uptake of water vapor, in which case the shelf life would be unreasonably short. There is a package type somewhere between these two extremes which satisfies most of the factors of economics which need be considered in the manufacture and distribution of products of this type. The degree of protection must be consist-

ent with packaging and distribution costs and consumer acceptability. The answer to this complex question is forthcoming only after an investigation of the present type.

A study of the results has shown that it is possible to obtain the necessary information in two ways: either the packaged article can be put on the shelf in the locality and at the time of year for which the information is required, or use can be made of weather bureau data, together with laboratory information on the characteristics of the package and the packaged product. The results indicate that the latter method is capable of yielding results sufficiently accurate for practical use. The former method, while capable of giving accurate shelf life values, is time-consuming and expensive, particularly if it is applied to all geographic locations at all times of the year.

These studies have shown that the shelf life of packaged cereals depends greatly upon the geographic location and upon the time of the year at which the packaged product is placed in that location. Because of these facts, differential packaging may be indicated where merchandising procedures can take advantage of such packaging. Thus, for instance, in Salt Lake City, Utah, the single liner package such as was studied in this paper would be more than adequate during any time of the year. On the other hand, in order to provide adequate shelf life in locations such as Houston, Texas, it is necessary to use a greater degree of protection than is afforded by the single liner package. In localities such as Chicago, the products could be packaged adequately in a single liner package for the greater part of the year, increasing the degree of protection as the more severe times of the year are approached.

An inspection of the curves of shelf life versus time of year (Figure 3) confirms the fact that storage life is also dependent, even though to a minor degree, upon the hygroscopic characteristics of the packaged product itself, a property which can be determined in the laboratory by moisture equilibrium studies.

Summary

A comparison of packaged cereal shelf life results obtained by field studies and by calculation shows that reliable data can be obtained by computation from weather bureau data for the locality, together with product and package data obtained under known laboratory conditions.

The agreement found between calculated and observed shelf life values is quite good in most cases. An explanation is given for the wide discrepancy noted with values for San Francisco.

The shelf life of a packaged cereal varies widely depending upon

the season, upon the section of the country in which the package is placed, and, to a lesser extent, upon the hygroscopic properties of the product itself.

Acknowledgment

The authors are indebted to Mr. T. R. Roberts for work in setting up and performing many of the calculations.

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1937 Permeability of membranes to water vapor with special reference to packaging materials. Miscellaneous Publication M-127, National Bureau of Standards, August 5.
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COMMUNICATION TO THE EDITOR

A Rapid Method for the Combined Determination of Thiamine and Riboflavin in Cereal Products

Received March 4, 1945

SIR:

Extraction with 20 ml of 25% KCl in 2% acetic acid has been employed for rapid determinations of thiamine [1] and riboflavin [2] in cereal products, a 1-g sample being taken for thiamine assay, whereas 0.5 g was used for riboflavin, in order to minimize the effect of sample size. By using aliquots of the same extract from the 0.5-g sample, and omitting permanganate decolorization for riboflavin, both vitamins in enriched flours are now assayed together as a routine procedure in this laboratory. Results are obtained within 70 minutes after receipt of the sample.

The question that arises is whether thiamine data for 0.5-g samples are sufficiently accurate. Results for routine determinations made in duplicate on 1-g and 0.5-g samples of 87 enriched flours are summarized below:

Sample size g	Mean μg/g	Standard error (single determination) μg/g
1.0	4.57	0.150
0.5	4.68	0.103

The mean values for all 87 samples show that significantly higher results were obtained with 0.5 g, but the small difference can be safely ignored, since it was reported [1] that the standard method yielded slightly higher results than the 1-g rapid method. The standard errors suggest that the 0.5-g samples give more reproducible results.

[1] Hoffer, A., Alcock, A. W., and Geddes, W. F. Cereal Chem. **20**: 717–729. 1943.
[2] Hoffer, A., Alcock, A. W., and Geddes, W. F. Cereal Chem. **21**: 524–533. 1944.

Our samples were taken off the streams going to the packing bins and were analyzed without any preliminary mixing. Apparently the vitamins were well dispersed throughout the flour. This may not always hold and it is suggested that if the results of replicate determinations indicate a lack of homogeneity, a part of the sample be well mixed before portions are weighed out for analysis.

A. HOFFER and A. W. ALCOCK,

Purity Flour Mills Ltd., Winnipeg, Manitoba

BOOK REVIEW

The Amino Acid Composition of Proteins and Foods. By Richard J. Block and Diana Bolling. 396 pp. Charles C. Thomas, Springfield, Ill. 1945. Price $6.50.

In the light of current manifestations of interest in the nutritional aspects of proteins and amino acids, intensified by war conditions, this book is most timely, and it will doubtless enjoy an enthusiastic reception. As a ready and convenient source of up-to-date information on the amino acid make-up of proteins and of foods (some of which has never before been published) and as a compact compilation of methods for the quantitative estimation of the individual amino acids, contained in one volume, the book is in a class by itself.

There are 11 chapters, eight of which are devoted respectively to the eight groups into which the authors have classified the amino acids on the basis of group similarities of composition and properties. Chapter 9 presents a discussion of general methods of protein hydrolysis and amino acid separations; chapter 10 gives summary tables showing percentages of the various amino acids in different proteins; while chapter 11 deals with the essential amino acid requirements of man.

Each amino acid is given adequate treatment as to special properties, methods of isolation and estimation, and stability toward different methods and conditions of protein hydrolysis. The subject matter is well organized and classified, and is presented clearly and concisely. The authors' numerous critical comments, many of which reflect a large background of personal experience, add greatly to the interest of the reader.

The authors have assembled, compiled, and tabulated all available information on the amino acid content of proteins and food stuffs and have calculated all percentages to a standard basis. In addition to the Summary Tables (chapter 10) there is, for each of the eight groups of amino acids, a full set of tables showing composition of proteins with respect to the amino acids of the group.

The bibliography contains 699 titles, and the references extend into the year 1943. There is an Author Index, and the Subject Index is unusually complete and comprehensive.

The general make-up of the book is attractive, and few typographical errors have been noted.

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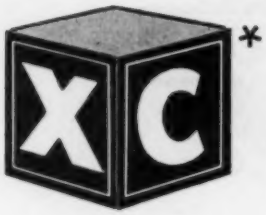

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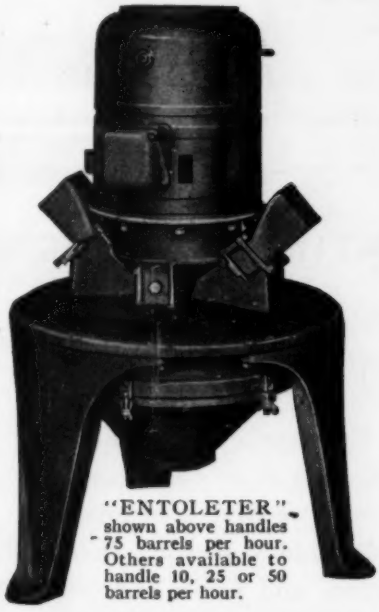

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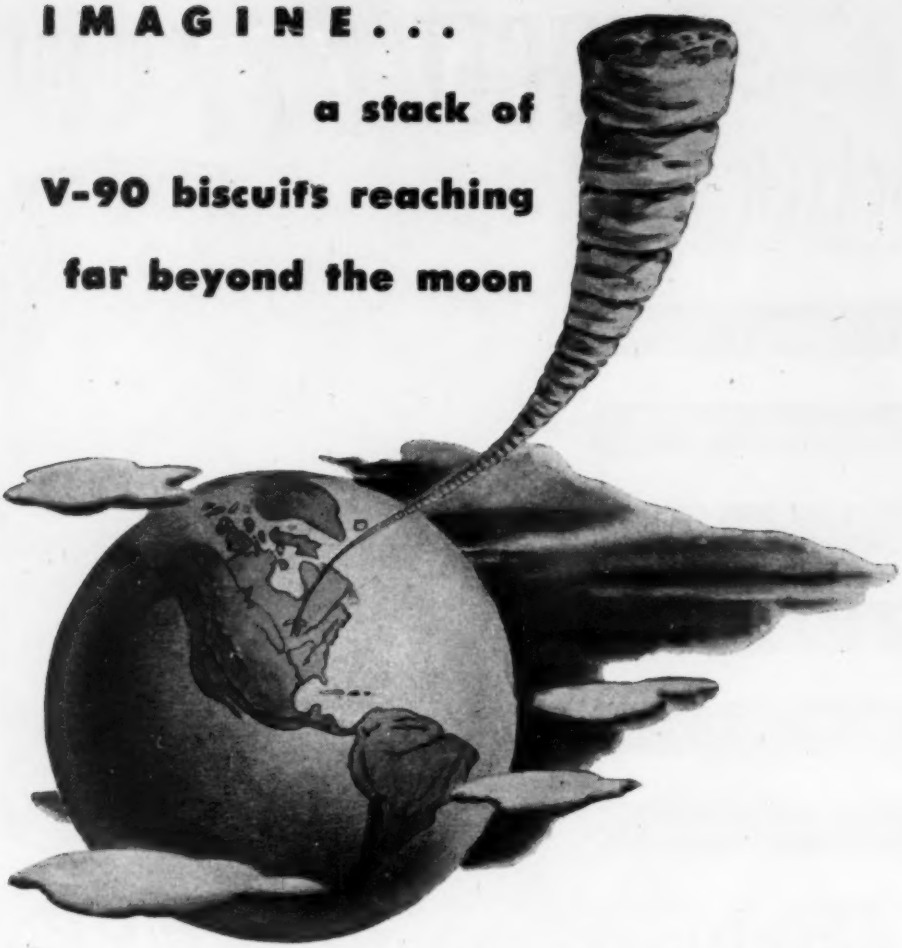

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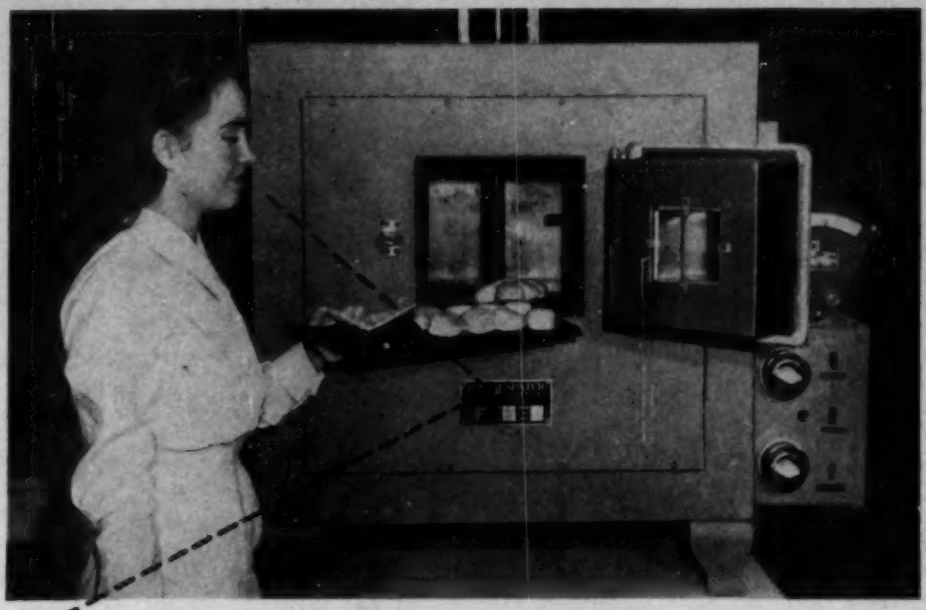

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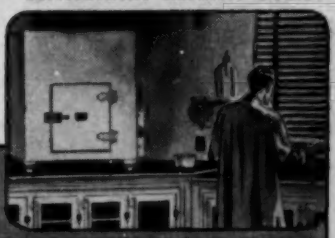

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